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A Study of the Calcium Complex of the Potassium Salt of Catechol-4-Sulfonate in Aqueous, Alkaline Media

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A STUDY OF THE CALCIUM COMPLEX OF THE POTASSIUM SALT OF CATECHOL-4-SULFONATE IN AQUEOUS, ALKALINE MEDIA

A thesis submitted by

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SUMMARY

This work was conducted to elucidate the interactions which occur between calcium and certain lignin fragments in kraft black liquors and to determine what role these interactions may ultimately have in the formation of calcium carbonate scale in black liquor evaporators. To this end, the complexation which occurs between calcium and the potassium salt of catechol-4-sulfonate (KC4S) was studied in aqueous, alkaline media.

The study was prompted by work done by Frederick and Grace which revealed that certain aromatic compounds (resembling lignin fragments found in black liquor) containing adjacent hydroxyl groups could effectively cause calcium carbonate scaling to occur in a bench scaling apparatus containing a synthetic liquor. This led them to hypothesize that such organic molecules formed a temperature sensitive chelate with calcium, and that this reaction was instrumental in the overall scaling mechanism.

The present study was conducted at temperatures ranging from 5 to 80°C in solutions of 0.92N ionic strength and at pH of 10 or greater. All of the work was done under nitrogen to prevent oxidation of the KC4S. The extent to which chelation occurred between calcium and KC4S was determined primarily from ultraviolet absorption measurements. Additional work was done using a calcium ion selective electrode.

Calcium formed a stable chelate with the totally dissociated KC4S (two ionized OH groups) with a 1:1 stoichiometric ratio. The stability constant of the chelate was determined from systems whose calcium:KC4S mole ratio ranged from 10:1 to 1:4. The log of the stability constant was determined to be 3.82 ± 0.04. No significant change in the log K was found in the temperature range investigated.

The actual distribution of calcium in the experimental system was found to be a complex function of temperature, base concentration and ionic strength rather than a straightforward relationship involving only temperature and chelate stability. The results of this study, however, clearly support Frederick and Grace's hypothesis that such organic compounds do interact with calcium under the prescribed conditions and that the net effect of heating these systems is to cause a shift from chelated to ionic (or scalable) calcium.

INTRODUCTION

ORIGIN AND PERTINENCE OF THE PROBLEM

The deposits which occur on the inside surface of black liquor evaporator tubes are one of the most persistent and troublesome problems in the recovery operation of alkaline pulp mills. The buildup of these "scales," as they are known in the industry, causes a continual reduction of heat transfer rate through the evaporator tube walls. They can be responsible for production bottlenecks, and they require mill shutdowns for cleaning.

Of the several different types of scale found in a recent survey of the alkaline pulp industry by Grace (1), calcium carbonate ($CaCO_3$) scales were one of the most common. Where they occurred, these scales governed short term evaporator performance.

Calcium carbonate scaling has generally been attributed to inorganic phenomena such as the inverse temperature-solubility behavior of calcium carbonate (2) or excess carbonate loading of the liquor (3). Results from a recent study conducted at the Institute by Frederick and Grace (4,5) provided empirical evidence that the organic constituents of black liquor play an important role in the formation of calcium carbonate scales.

Frederick and Grace observed that synthetic liquors composed entirely of inorganic constituents (sodium carbonate, sodium hydroxide and calcium oxalate) would not form scale when heated in a bench scaling apparatus. However, the addition of either the lignin component of an actual black liquor or certain lignin-related model compounds would cause significant scaling to occur. The model compounds in Fig. 1 were found to promote calcium carbonate scaling in the order noted.

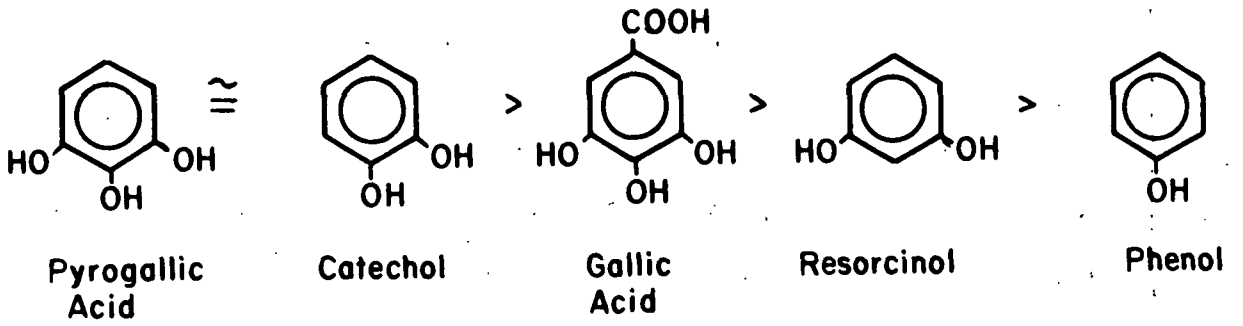

Figure 1. Relative Abilities of Selected Organics to Sensitize Scaling Mechanism

These results served as the basis for their postulate that certain lignin-related organic compounds, specifically aromatic molecules with adjacent ring hydroxyl groups, could effectively solubilize calcium by forming a chemical complex with it in black liquor systems. They further hypothesized that these complexes were thermally unstable and that they dissociated at higher temperatures, releasing ionic calcium that formed scale with the abundant carbonate ion already in the liquor.

Frederick and Grace found that the mill black liquors with which they had worked had soluble calcium levels which were several orders of magnitude higher than what would be predicted based on the solubility product of calcium carbonate. This was considered to be supporting evidence for their postulated mechanism. Additional evidence came from actual mill trials where black liquor which was heated prior to entering evaporator tubes was found to scale to a much lesser extent than untreated liquor (6,7). It was believed that this preheating of the liquor caused the complex to dissociate, so that the calcium precipitated harmlessly from solution as calcium carbonate particulate.

COMPLEXES AND CHELATES

GENERAL

A complex (or coordination compound) can be defined as a compound which results when a metal ion combines with an electron donor (8). A chelate is a special type of complex which occurs when a metal ion combines with two or more electron donating groups on the same molecule. Some common examples of chelates are hemoglobin, chlorophyll and the calcium chelate of ethylenediaminetetraacetic acid (EDTA).

Almost all of the metals of the periodic chart undergo complex formation with at least one type of an electron donor. The transition metals, however, are generally considered to have the strongest tendency to form complexes. They have been shown to complex with a large number of ligands (molecules with donating groups) to form a wide variety of complexed species.

CALCIUM COMPLEXES

Calcium and the other alkaline-earth and alkaline metals generally form less stable complexes than do the transition metals. Furthermore, they do not react with such a wide variety of ligands and typically complex only with those containing highly electronegative donor groups such as amines, ammonia, water or ions like phosphate, sulfate or carboxylate. This is largely a consequence of their electronic structures and is characteristic of metal ions in which the outermost shell contains 2 or 8 electrons (9).

Most of the studies which have been done with calcium as a complexing or chelating metal have been with regard to its role in biological systems. A thorough review of this work has recently been published (10). The emphasis of most of

this work has been on either proving the existence of such complexes, or on determining their structure, with little emphasis placed on determining their stability constants.

Calcium's ability to complex with organic ligands containing adjacent hydroxyl groups is well established. It has been shown to form chemical complexes with the carbohydrates (11,12) and ethylene glycol (13) in aqueous systems at or near neutral pH.

The first evidence that aromatic molecules containing adjacent hydroxyl groups would complex with calcium was presented by Malát, Suk and Ryba (14) in 1954, who found that a deep violet color resulted when catechin violet (Fig. 2) was added to an alkaline solution containing calcium. Shortly thereafter Murakami (15) presented evidence from potentiometric titrations to show that both 4-carboxy catechol and catechol-4-sulfonate form calcium complexes in dilute aqueous, alkaline solutions. He reported the stoichiometry of these complexes to be both 1:1 and 1:2 (calcium:ligand). More recently, Morita (16) isolated a 1:2 calcium (bromide) catechol complex from neutral, aqueous solutions by evaporation of a dilute solution containing calcium bromide and catechol.

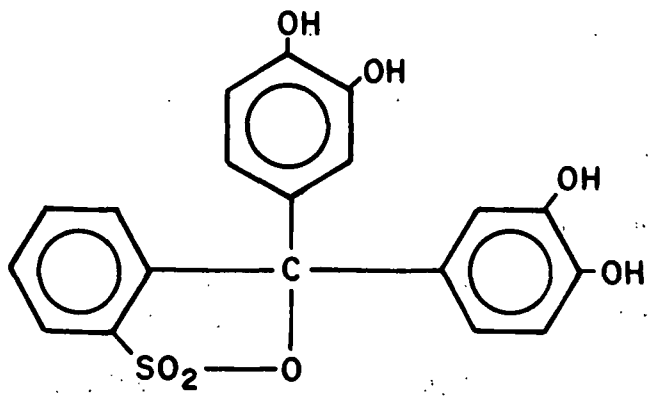

Figure 2. Catechin Violet Forms a Deep Violet Color when Added to Alkaline Solutions Containing Calcium Ions

EQUILIBRIUM REACTIONS

When considering reversible reactions of the type

$$A + B \rightleftharpoons C + D \tag{1}$$

the tendency of the reaction to go to completion can be quantitatively expressed by an equilibrium constant (K_{eq}) such that (17)

$$K_{eq} = \frac{[C] \cdot [D]}{[A] \cdot [B]} \tag{2}$$

The reactants and products can be expressed as either concentrations or activities. The activity of any species can be related to its concentration through the use of an activity coefficient such that

$$\{A\} = \gamma_A [A] \tag{3}$$

where:

$\{A\}$ = activity of A

γ_A = activity coefficient of A

[A] = concentration of A.

When K_{eq} is expressed in terms of equilibrium concentrations [as it is in Eq. (2)] it is referred to as a stoichiometric or concentration equilibrium constant. When the equilibrium constant is expressed in terms of the reactants' and products' activities, it is known as a thermodynamic equilibrium constant. When both activities and concentrations are used to express the equilibrium constant, it is known as a mixed constant. Mixed equilibrium constants are commonly used to define equilibrium reactions determined on the basis of pH measurements (as known concentrations of reactants are used, and pH measurements determine hydrogen ion activity).

The concentration and mixed equilibrium constants (K_c and K_m, respectively) are related to the thermodynamic equilibrium constant, K_t by Eq. (4).

$$K_t = \frac{\gamma_H [H]\ \gamma_A [A]}{\gamma_{HA}\ [HA]} = K_c \frac{\gamma_H\ \gamma_A}{\gamma_{HA}} = K_m \frac{\gamma_A}{\gamma_{HA}} \qquad (4)$$

At very low solution concentrations, the activity coefficients tend to unity, and the values of K_c and K_m approach K_t. The rationale for working in very dilute solutions or at a known, constant ionic strength stems from the dependence of the activity coefficients on the ionic strength. Clearly, data taken at different ionic strengths cannot be used collectively for the determination of an equilibrium constant.

STABILITY CONSTANTS

General:

A stability constant is an equilibrium constant which quantifies the stability of a metal complex. The following equation can be used to define the stoichiometric stability constant of a complex ML_n.

$$K_n = \frac{[ML_n]}{[ML_{n-1}]\ [L]} \qquad (5)$$

There are a variety of experimental methods by which stability constants can be determined, and they are discussed at some length in texts by Rossotti and Rossotti (18) and Beck (19). Among these are methods based on potentiometric, conductometric, polarographic and spectroscopic measurements. There are also methods which are based on measurements of the physical and colligative properties of the solutions where complexation is occurring. The recent development of ion-selective electrodes offers a new potentiometric method of determining stability constants.

There are many different numerical methods available for treating the experimental data. They range from simple graphical treatments to highly complex numerical solutions that require a high speed computer. The text by Rossotti and Rossotti thoroughly discusses the theory and application of most of the methods. More recent papers by Field and McBryde (20) and Bond (21) discuss some of the newer, more sophisticated techniques which require a computer for data analysis.

Application to this Study:

Analytical Technique

While a wide variety of analytical techniques are available for determining stability constants, the requirements for this study were best met by an ultraviolet spectroscopic technique. It was selected for the following reasons.

1. It permitted the analysis of samples with concentrations of 3.2×10^{-4} molar of the model compound. Concentrations of the reacting species had to be kept low, due to the limited solubility of calcium in alkaline, aqueous systems.

2. Ultraviolet absorption data could be conveniently taken without exposing the samples to oxygen. This was accomplished by preparing the samples in a glove bag and filling cuvettes which were then tightly capped in the bag. This prevented the oxidation of the model compound which occurs readily when catechol-type compounds in alkaline solution are exposed to air.

3. It was convenient to analyze the samples at temperatures ranging from 5° to 80°C using the UV technique, as the spectrometer was equipped with jacketed sample holders capable of maintaining the temperature within 0.1°C.

Absorption Measurements and Beer's Law

Quantitative determinations made on the basis of optical measurements are done so with the understanding that the Lambert-Beer Law (hereafter referred to as Beer's Law) is being adhered to by the absorbing species. Beer's Law can be expressed as:

$$A = \varepsilon bc = \log(1/T) = \log(P_o/P) \qquad (6)$$

where:

A = absorbance

ε = molar absorptivity, liters/(mole centimeter)

b = cell path length, centimeters

c = concentration, moles/liter

T = transmittance

P = transmitted radiant power

P_o = incident radiant power

The test for conformity of a system to Beer's Law can be made by plotting absorbance vs. concentration for several samples which differ only in the amount of the absorbing component which they contain. (Temperature, pH, and ionic strength of the samples must be the same.) A straight line plot indicates adherence.

A more detailed discussion of optical measurements will not be included here as it can be found in at least several places in the literature (22-24). Also, a thorough discussion regarding the use of ultraviolet and visible spectroscopic data for determining stability constants can be found in Rossotti and Rossotti. The only stipulations involved with using the method are that Beer's Law must hold and that a wavelength must exist where the absorptivity of the complex in question differs appreciably from the absorptivity of other species in the system.

Method of Data Gathering

Once an analytical wavelength has been chosen, collection of the data consists of measuring the pH and the absorbance at the analytical wavelength of a carefully prepared group of samples. These samples are at constant ionic strength and temperature and contain the same concentration of model compound but different concentrations of metal and base. The data collected in this manner are then used in a series of mass balance and equilibrium equations to determine the stability constant(s) of the complex(es) in the system in a manner that will be described in the following section.

Numerical Methods

The numerical method by which the stability constant of the complex in this experimental system was derived from the data involves the simultaneous solution of several linear and nonlinear equations. This method has not been used extensively in the past, primarily because its use requires a high speed computer. The advantages of this particular approach are that it is straightforward and it is amenable to very complex systems. It was chosen for this study because it was not known how many complex species existed in the system, and its flexible capacity was therefore desirable.

One difficulty encountered in using the method of simultaneous equations to solve equilibrium equations is that the system can become overdefined mathematically. This occurs when there are more equations to be solved than there are unknown quantities. It is a consequence of the fact that new mass balance and equilibrium equations can be formulated for each experimental data point; but as some unknowns are equilibrium constants, they appear only once. The result of this is that there can be multiple solutions to the equations.

This problem can be dealt with by determining a 'best fit' solution. In essence, this involves using some criterion for determining one solution that comes closest to solving all of the equations. For this study, the best fit solution was determined on the basis of a least squares fit.

As it was not known what complex species existed in the experimental system, initial assumptions had to be made. A data set which gave the least squares best fit to the experimental data was calculated on the basis of each assumption. The assumption which gave the (statistically significant) best fit to the data was considered to be the one which best defined the system. (This is based on the premise that the correct system will give the best fit to the experimental data.)

While this method was used to determine both the structures and stability constants of the complexes which form between calcium and KC4S, it was not intended to be a rigorous proof of the composition of the experimental system. The exact manner in which this method was employed is discussed in the Experimental section.

Example — One-complex System

If it was assumed that only one complex, ML (one metal ion combined with one ligand molecule) existed in the system, then the following mass balance and equilibria equations could be formulated.

$$[T_M] = [M] + [ML] \tag{7}$$

$$[T_L] = [LH] + [L] + [ML] \tag{8}$$

$$K_{LH} = \frac{\{H\} \cdot [L]}{[LH]} \tag{9}^*$$

*Note that all quantities except $\{H\}$ are expressed as concentrations and that therefore, K_{LH} is a mixed dissociation constant. Also, the charges on the species have been omitted for simplicity.

$$K_{ML} = \frac{[ML]}{[M] \circ [L]} \tag{10}$$

$$A = [LH]\,\varepsilon_1 + [L]\,\varepsilon_2 + [ML]\,\varepsilon_3 \tag{11}$$

where:

$[T_M]$ = total metal

$[T_L]$ = total ligand

$[M]$ = concentration of ionic metal

$[ML]$ = concentration of complexed species

$[LH]$ = concentration of molecular (or partially dissociated) ligand species

$[L]$ = concentration of dissociated ligand species

$\{H\}$ = activity of hydrogen ion

K_{LH} = dissociation constant for ligand species

K_{ML} = stability constant of complex

ε = molar absorptivity of respective species.

The total metal (T_M) and the total ligand (T_L) concentrations for each sample are known, and the absorbance (A) and hydrogen ion activity are measured. K_{LH}, ε_1, and ε_2 can be determined separately. This leaves [M], [ML], [LH], [L], K_{ML} and ε_3 as the unknown quantities making five equations and 6 unknowns. By considering two data points simultaneously, however, there will be ten equations (two each of the above) and ten unknowns; [M], [M]'; [LH], [LH]'; [L], [L]', [ML], [ML]'; K_{ML} and ε_3.

It can readily be seen that if 35 data points were taken, there could be as many as 595 ((35!-33!)/2!) slightly different K values calculated. (If 2 complexes were assumed, over 52,000 individual calculations would have to be made for 35 data points, as four data points are needed for each calculation).

For the best fit solution, these same equations are used, but values for K_{ML} and ε_3 are assumed, and A is treated as an unknown to be calculated. This way, for a given data point, $[T_M]$, $[T_L]$, K_{LH} and $\{H\}$ are treated as knowns and ε_3 and K_{ML} are assumed. What results is 35 calculated "data" points for which the pH value is correct (as measured) but for which the absorption values are calculated, based on the assumption that one complex exists with the stability constant and molar absorptivity values which have been input.

Each calculated data point is then compared to the corresponding experimental data point. The square of the difference between the calculated and measured absorption is determined for each point and these quantities are summed. The total is labeled S so that:

$$S = \sum_{i=1}^{35} (A_{ci}-A_{mi})^2 \qquad (12)$$

where:

A_c = calculated absorption

A_m = measured absorption

The smaller the value of S is, the better the fit of the calculated data to the real data and therefore the better the assumed values of K_{ML} and ε_3. The object is then to minimize S. This can be accomplished with a computer program that is designed to find the minimum of a function of several variables.

ACID DISSOCIATION CONSTANTS

General:

Acid dissociation (or acidity or ionization) constants are equilibrium constants which are used to express the degree to which a particular acid will dissociate or ionize in solution. The stoichiometric acid dissociation constant can be defined by the following equation.

$$K_{a(c)} = \frac{[H] \cdot [A]}{[HA]} \qquad (13)$$

where:

[H] = concentration of hydrogen ion

[A] = concentration of dissociated acid

[HA] = concentration of undissociated acid.

Acid dissociation constants are commonly determined using potentiometric titrations, which yield mixed dissociation constants as discussed on page 7 and shown in Eq. (14).

$$K_{a(m)} = \frac{\{H\} \cdot [A]}{[HA]} \qquad (14)$$

An acid dissociation constant is usually a very small number and is therefore more conveniently expressed as a pKa which is the negative log of K_a. The pKa's for most common organic acids in aqueous solutions have been determined under at least one set of conditions and can be found in the literature. At least two texts have been published which collectively contain pKa values for over 5000 organic acids (25,26).

The pKa value for a particular organic acid can usually be determined by a simple potentiometric titration procedure. The method is not always suitable however, and when it is not, there are several other techniques which can be employed.

Albert and Serjeant (27) have reported a method for determining pKa values greater than 11 using ultraviolet absorption measurements. The only stipulations are that Beer's Law must hold, that the ionic species exhibit appreciably different absorptivities at at least one wavelength, and that the molar absorptivity of each ionic species at the chosen wavelength be known [Eq. (15)].

$$pKa = pH \pm \log \frac{\varepsilon_1 - \varepsilon}{\varepsilon - \varepsilon_0} \qquad (15)$$

where:

ε_0 = molar absorptivity of less ionized species

ε_1 = molar absorptivity of more ionized species

ε = molar absorptivity of a mixture of the species.

However, it is not always possible to directly measure the molar absorptivity of a given compound. When the pKa of a compound is very high, it is not possible to measure the molar absorptivity of the more ionized species without going to a very high ionic strength. Also, if the compound has two protons which dissociate in similar pH regions, it may not be possible to isolate the partially dissociated species.

Application to this Study:

Under the experimental conditions employed in this study, the second* acid dissociation constant of KC4S is quite high (11.7-12.7). Therefore, an alternate method of treating the data was employed. This method is based on Beer's Law [expressed in Eq. (6), page 10).

If the path length (b) of the cuvettes used is 1 cm, and both a partially dissociated (one ionized hydroxyl group) and a totally dissociated species are present, Eq. (6) can be rewritten:

$$A = [LH]\ \varepsilon_1 + [L]\ \varepsilon_2 \qquad (16)$$

*KC4S has two acidic protons on adjacent hydroxyl groups. The first hydroxyl proton has a pKa of about 7 or 8, while the second pKa is much higher.

At higher pHs*, the total ligand concentration can be expressed as:

$$[T_L] = [LH] + [L] \tag{17}$$

Equations (16) and (17) can be combined to give:

$$A = ([T_L] - [L])\ \varepsilon_1 + [L]\ \varepsilon_2 \tag{18}$$

Rearranging:

$$A = (\varepsilon_2 - \varepsilon_1)\ [L] + \varepsilon_1\ [T_L] \tag{19}$$

Absorption can be plotted as a function of the concentration of the totally dissociated ligand ([L]) to give a line of slope $(\varepsilon_2 - \varepsilon_1)$ and intercept $\varepsilon_1\ [T_L]$.

Samples at the same ionic strength and temperature and containing the same total ligand concentration and in a pH range close to the second pKa should yield a straight line plot of A vs. [L]. This can be exploited with a simple computer program which determines the best value for pKa_2 by determining which pKa_2 value causes the samples to come closest to falling on a straight line.

*At pHs above 10 KC4S exists in only two forms. One form has one hydroxyl proton associated with it [LH]; the other has lost both hydroxyl protons [L].

THESIS OBJECTIVES

The purpose of this study was to determine how catechol or a similar lignin-related model compound could affect the distribution of calcium in an aqueous, alkaline system. Emphasis was placed on determining the structure and stability of the complex(es) that form as well as on determining the effect that temperature has on the ability of the model compound to affect calcium distribution in such a system.

The first objective of the study was to show that calcium and the model compound actually form a complex. Once this was established, the second objective was to develop a means of quantifying the model compound's affinity for calcium throughout a temperature range. This was to be done through the use of stability constants. The determination of the stability constants of the calcium complex(es) of the model compound at several temperatures thus became the second objective of this study.

With the second objective completed, it became possible to define the behavior of any species of the system as a function of the experimental variables. The final objective of this study was then to define the behavior of ionic (or scalable) calcium with respect to temperature within the range of experimental conditions employed.

EXPERIMENTAL APPROACH

One of the most challenging aspects of this study was to design an experimental program without knowing the chemical or structural nature of the complex. This made it necessary to consider techniques that could be employed at neutral and high pHs and at extremes of metal:ligand ratios. Additional challenges were presented by the low solubility of calcium, the tendency of catechol-type compounds to oxidize, and the ability of calcium to exist as a hydroxide $(CaOH)^+$ at higher pH's (28).

SELECTION OF THE MODEL COMPOUND

Catechol was originally chosen as the model compound to be used in this study because it was one of the lignin-related model compounds which Frederick and Grace had shown would initiate the scaling reaction in their bench scaling apparatus. Catechol was replaced by the potassium salt of catechol-4-sulfonate (KC4S) early in the study, however (Fig. 3).

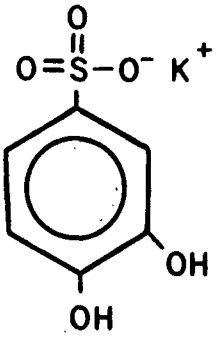

Figure 3. The Potassium Salt of Catechol-4-Sulfonate (KC4S)

KC4S was substituted as the model compound because of some difficulties that arose which were felt to relate to the solubility of either catechol or the complex. The addition of the sulfonate group assured the solubility of the free ligand and the complex (29) while not interfering in any complexing reactions (30). It should be noted that the sulfonate group on KC4S is completely ionized under all of the experimental conditions employed in this study. Therefore, further comments

regarding the dissociation of KC4S pertain only to the dissociation of the acid protons from the hydroxyl groups.

SELECTION OF THE ANALYTICAL TECHNIQUE

Initially, an analytical method for determining the stability constant(s) of the complex(es) was proposed which relied on potentiometric measurements made with a pH and a calcium ion selective electrode. The calcium electrode is a relatively new analytical tool which measures ionic calcium from a potential which develops across a porous, organophilic membrane, shown in Fig. 4. The potential is measured against a constant reference potential (31) and converted to ionic calcium concentration by the Nernst equation.

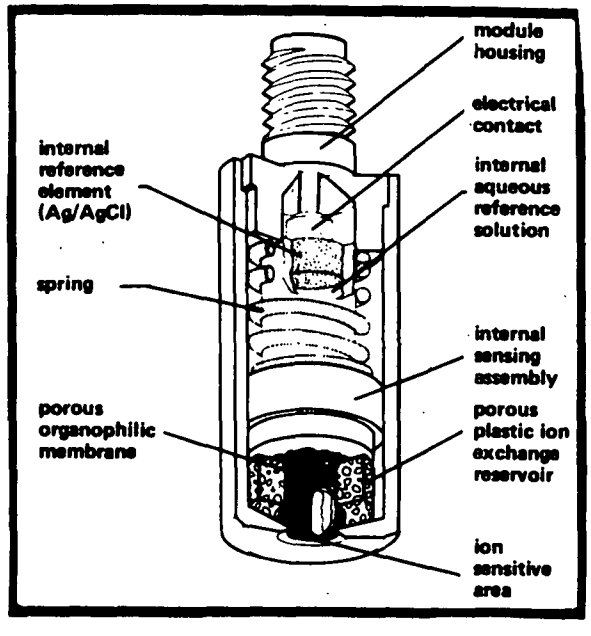

Figure 4. Diagram of the Sensing Module of the Calcium Ion Selective Electrode

Some problems* were encountered with the performance of the calcium electrode at higher temperatures and over extended time periods, however, which caused some concern regarding its use as the primary analytical technique. Preliminary tests

*Potential readings taken using the electrode tended to change with time (or drift). Also, the electrode gave erratic responses at temperatures above 40°.

showed that the ultraviolet spectroscopic technique would give more reliable results across a wider range of experimental conditions. It was therefore decided to employ the ultraviolet spectroscopic technique as the principal analytical method and to use the calcium ion selective electrode on a limited basis to substantiate the results obtained from the UV method.

RESULTS AND DISCUSSION

pKa DETERMINATIONS

Theory:

KC4S has two acidic protons. The proton meta to the sulfonate group comes off at a lower pH (15). The pKa of the second proton is significantly higher than the first because of positive inductive effects and because of the affinity of the hydroxide anion for the remaining proton (32) diagrammed in Fig. 5.

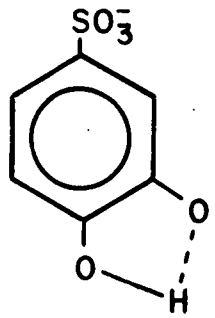

Figure 5. Proposed Structure of the Partially Dissociated KC4S

Prior to determining the acid dissociation constants of KC4S using the ultraviolet spectroscopic technique, its adherence to Beer's Law was checked. It was found to obey Beer's Law at concentrations ranging from 4.0×10^{-5}M to 4.8×10^{-4}M. (The initial concentration of KC4S used in all of the samples prepared for the ultraviolet absorption analysis was 3.2×10^{-4}.)

pKa1:

The first acid dissociation constant of KC4S was determined by both a potentiometric and the spectroscopic technique at a constant ionic strength of 0.1N (KNO_3) from 20° to 80°C. The results were in good agreement with each other, and with the values that have been reported in the literature (15,33,34). As the dissociation of the proton meta to the sulfonate group was found to occur at such

a low pH as not to affect the calcium-KC4S reactions, results from these experiments will not be included here, but can be found in Appendix II.

pKa2:

The second acid dissociation constant of KC4S was found to be quite high at 0.1N ionic strength (12.84 at 20°C). This presented somewhat of a problem, as operating at a constant ionic strength of 0.1N imposed a pH ceiling of about pH 13 at 20°C. This made it impossible to gather data at high enough pH so that solutions of KC4S would be predominantly totally dissociated at higher temperatures. This in turn prevented accurate determinations of the pKa2 from being made at 0.1N at 40-80°C. For this reason, it was decided that this study would be conducted at higher ionic strength; 0.92N (KCl) was chosen as a matter of convenience.

The analytical wavelength that was chosen for the pKa determinations was 255 nm, as that is where the spectra of the different ionic forms of KC4S are most different. Some pKa determinations were also done at 240 nm, as that is the wavelength where the calcium work was done. UV absorption spectra of the three ionic forms of KC4S are shown in Fig. 6.

The results from these determinations are shown in Table I. The computer plots of the data from which the pKa2 values were actually calculated are contained in the Appendix.

Confidence limits of 95% were determined for the pKa2 value reported at 20°C and 0.92N ionic strength which was calculated from the data taken at 240 nm. These data were chosen as they gave a typical fit to the calculated pKa2 line. The method used is a statistical determination and is elaborated on in the Appendix. The 95% confidence limits were determined to be 12.26 and 12.48, or 12.37 ± 0.11.

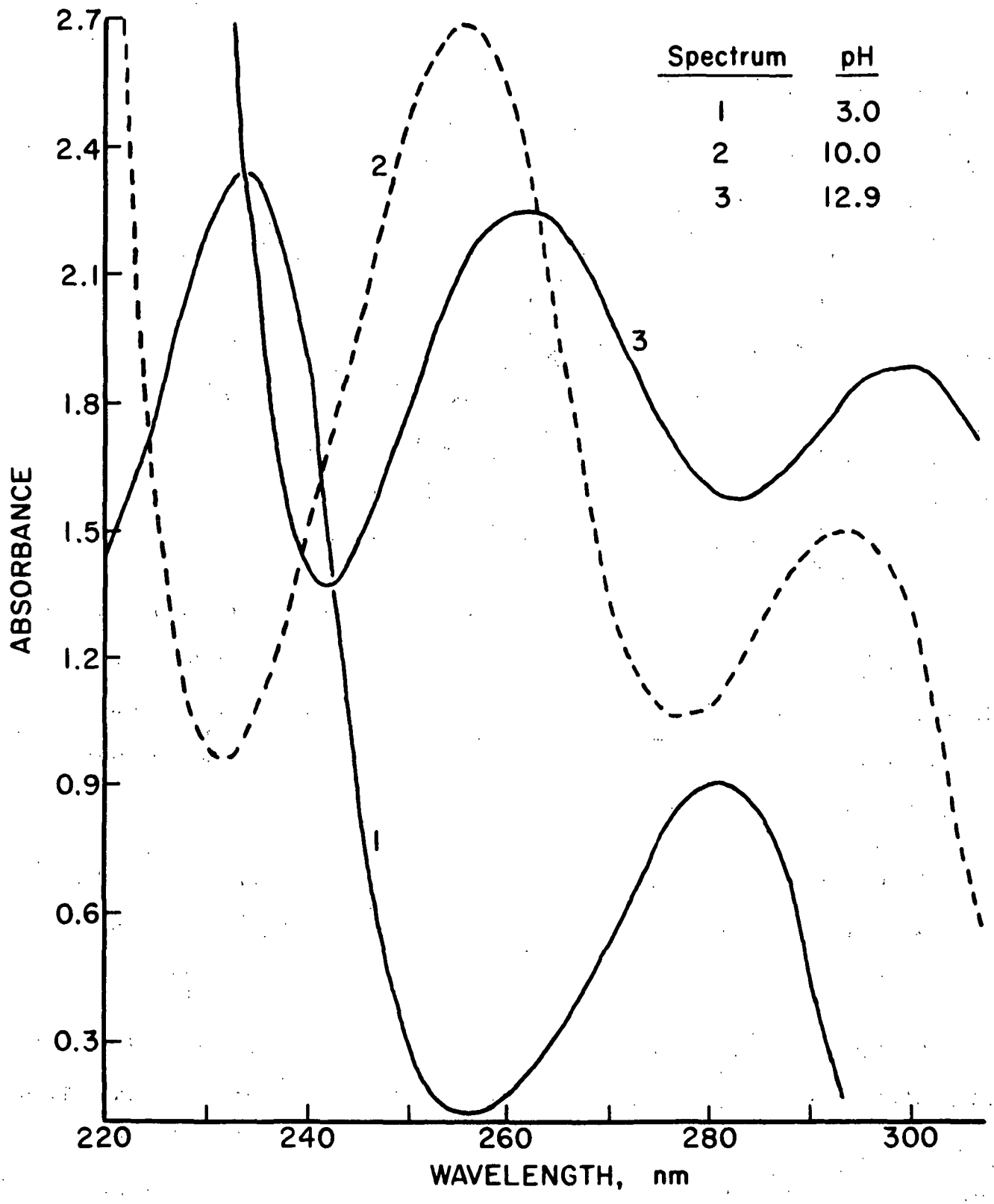

Figure 6. Ultraviolet Absorption Spectra of KC4S (0.00032M) at 25°C. Spectrum 1, Neither Hydroxyl Group is Ionized; Spectrum 2, Hydroxyl Meta to Sulfonate is Ionized; Spectrum 3, Meta Hydroxyl is Ionized, Para Hydroxyl is about 60% Ionized

TABLE I

ACID DISSOCIATION CONSTANTS OF KC4S AS DETERMINED UNDER NOTED CONDITIONS

Temperature	Ionic Strength	pKa2 (240 nm)	pKa2 (255 nm)	Value Used
5	0.92N (KCl)	12.65	--	12.65
20	0.92	12.37	12.28	12.32
20	0.10	--	12.84	12.84
40	0.92	12.04	12.05	12.05
60	0.92	--	11.81	11.81
80	0.92	--	11.69	11.69

There are no values reported in the literature for the pKa2 at 0.92N ionic strength. Three workers have reported values for pKa2 at 0.1N ionic strength. The values determined are 12.16 at 30°C (15), 12.20 at 25°C (33) and 11.6 and 12.2 at 25° (34). The first two workers used a potentiometric titration technique (using a glass electrode) while the third used the hydrogen electrode and an ultraviolet spectroscopic technique.

The discrepancy between the value found in this study and those reported in the literature (12.8 vs. 12.2) is apparent. An additional run was done using potassium nitrate (KNO_3) as the ionic strength adjuster (as in the literature). The pKa2 value was determined to be 13.00 from these data. Both sets of data are plotted in Fig. 7. While there is not particularly good agreement between these determinations, it is readily apparent that the maximum change in absorption over the change in pH occurs beyond the literature value of pH 12.2.

The pH measurements taken in the present study were done using a high pH electrode which was calibrated using a high pH standard prepared according to NBS methods (35). None of the earlier workers reported taking such precautions. Use

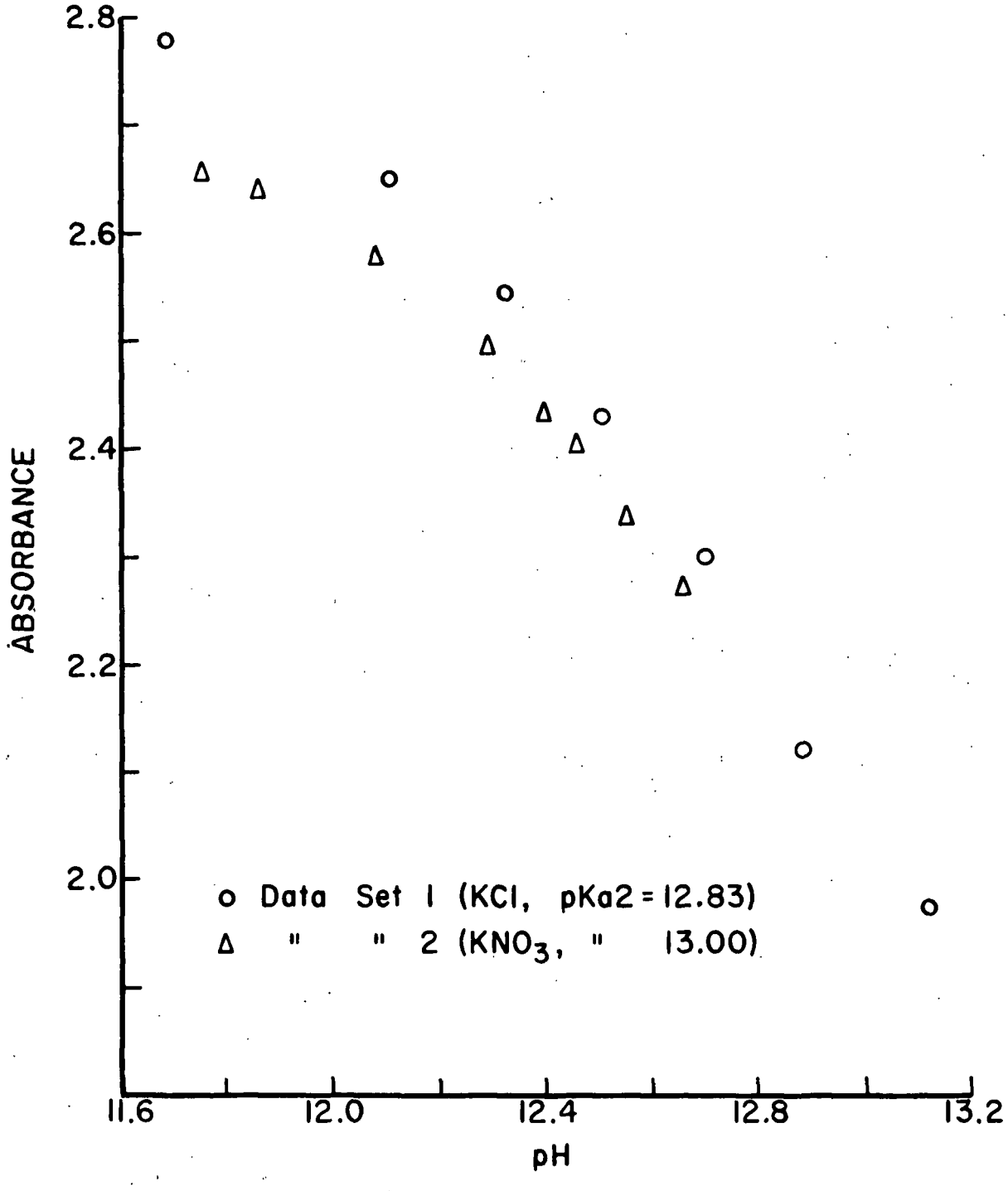

Figure 7. Plot of Data Taken in Two Separate Experiments to Determine the pKa2 of KC4S at 0.1N Ionic Strength and at 20°C. (λ = 255 nm, KC4S Concentration = 0.00032M)

of a standard pH electrode at high pHs can cause low readings due to the alkaline error. For example, use of a Beckman standard pH electrode at pH 13 will give a reading that is low by about 0.5 pH units (35).

Albert and Serjeant (27) specifically recommend that potentiometric titration measurements not be used for determining pKa values higher than 11. pKa Values determined by ultraviolet spectroscopic methods are equally susceptible to alkaline error, as they are based in part on pH measurements. With regard to the determination done using the hydrogen electrode, Lingane (36) has listed a variety of problems which cause the hydrogen electrode to be both difficult to work with, and at times, inaccurate.

The discrepancies between the results of this study and those of earlier studies are very likely the result of improved technology, particularly with regard to pH electrodes. pH Measurements made in the course of this study using the equipment and techniques described in the Experimental section were found to be both stable and reproducible.

The pKa2 values determined at 0.92N ionic strength are plotted in Fig. 8. Thermodynamically, the relationship between K and T is expressed by the Gibbs-Helmholtz equation:

$$\frac{d\ln K}{d(1/T)} = \frac{-\Delta H}{R} \qquad (20)$$

THERMODYNAMICS OF THE DISSOCIATION OF THE SECOND ACIDIC PROTON FROM KC4S

Thermodynamic quantities are generally derived from and pertain to systems of infinite dilution. As it was necessary to conduct this study at relatively high ionic strength (0.92N) the values calculated here are only approximations of what they would be at infinite dilution.

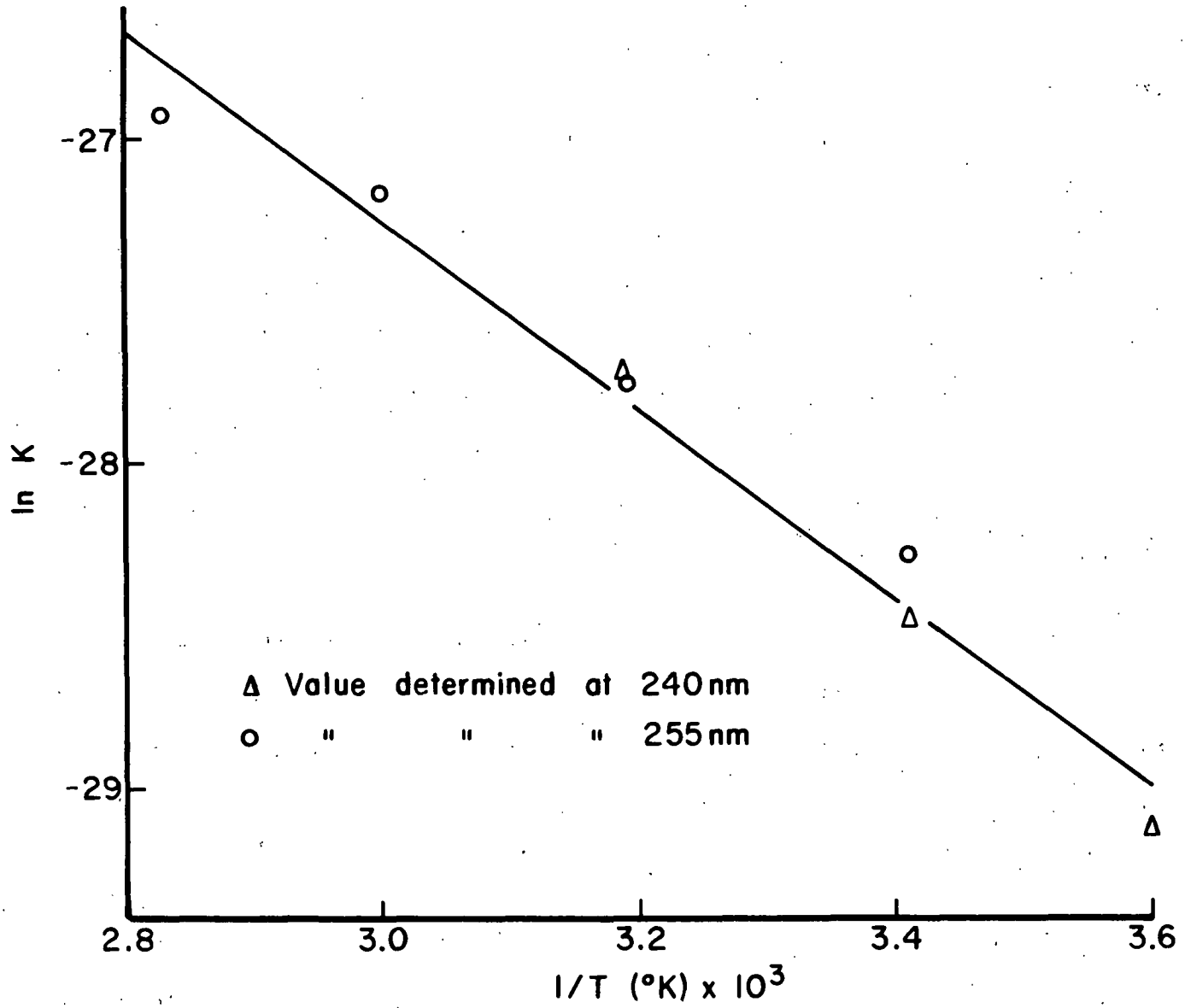

Figure 8. Plot of ln K versus 1/°K for the Second Acid Dissociation Constant of KC4S

The approximately linear relationship between ln K and 1/T seen in Fig. 8 is not unexpected, so long as ΔH is constant over the temperature range, which it usually is over moderate ranges (37). The heat of reaction $(\Delta H_{0.92})^*$ can be determined from the slope of the line through the points plotted in Fig. 8. From a linear regression analysis it is calculated to be:

*The subscript 0.92 refers to the ionic strength at which the data were taken.

$$-\Delta H_{0.92}/R = -\Delta H_{0.92}/8.314 \frac{\text{Joules}}{^\circ\text{K mole}} = 2{,}880^\circ\text{K} \quad (21)$$

$$\Delta H_{0.92} = 8.314 \frac{\text{Joules}}{^\circ\text{K mole}} \times 2{,}880^\circ\text{K} = 24{,}000 \frac{\text{Joules}}{\text{mole}} \quad (22)$$

The positive value for $\Delta H_{0.92}$ indicates that the reaction is endothermic, which is to be expected for a bond-breaking reaction (38).

The free energy change associated with the dissociation of the second proton from KC4S can be calculated at each experimental temperature from Eq. (23).

$$\ln K = -\frac{\Delta G}{RT} \quad (23)$$

The entropy change can be calculated from Eq. (24).

$$\Delta G = \Delta H - T\Delta S \quad (24)$$

The results from these calculations are shown below in Table II.

TABLE II

THERMODYNAMIC QUANTITIES ASSOCIATED WITH THE DISSOCIATION OF THE SECOND PHENOLIC PROTON FROM KC4S

Temperature	$\Delta G_{0.92}$(KJ/mole)	$\Delta S_{0.92}$(J/mole °K)
5	67.4	-156
20	69.2	-154
40	70.8	-150
60	75.3	-154
80	79.1	-156

Entropy changes for dissociation reactions are usually positive (38). It is not known for sure why the values found in this study were negative. One possible explanation is that the water molecules surrounding the totally dissociated KC4S become structured (39). The consistency of the entropy values from 5° to

80°C could be anticipated based on the fact that ΔH is nearly independent of temperature in that same range (38).

The change in the values for the free energy of formation seen in Table II can be attributed to Eq. (24). If ΔH and ΔS are constant, then as T increases, $-T\Delta S$ becomes increasingly larger (ΔS is negative) and ΔG therefore becomes larger.

STABILITY CONSTANT DETERMINATIONS

PRELIMINARY EXPERIMENTS

Experiments with Catechol:

Initially the calcium ion-selective electrode was chosen to be the primary analytical technique to be used in this study, and catechol was chosen as the model compound. When catechol was added to an aqueous, alkaline system containing small amounts of dissolved calcium, however, the electrode first indicated a sharp decrease in the ionic calcium level (which would be expected if complexation were occurring) followed by a gradual return (over several minutes) to the original calcium level. Subsequent experiments involving the use of the calcium electrode in systems containing catechol gave equally erratic results. A check of the literature revealed that several phenolic compounds, among them resorcinol, had been found to have undesirable interactions with the calcium electrode (40).

It was suggested that this problem could be overcome with the addition of a sulfonate group to the catechol molecule (41). Improved electrode response was achieved in subsequent trials using the potassium salt of catechol-4-sulfonate. It was therefore substituted for catechol as the model compound.

Experiments with the Calcium Electrode:

Although at least two workers (42,43) have reported using the calcium ion selective electrode to determine stability constants, it was checked using a calcium chelate of known stability to insure its accuracy. The chelating agent chosen was citric acid, and its calcium complex has been investigated by several workers (44-47). The average value determined from nine separate experiments for the log of the stability constant of the calcium-citric acid complex using the calcium electrode was 3.39 and the range was from 3.29 to 3.48 (at 0.1N ionic strength and at ca. 25°C). Literature values range from 3.15 to 3.50.

The calcium electrode responded adequately in systems containing calcium and KC4S at room temperature. It was used only as a back-up analytical technique because of its limited pH range (upper limit of pH 11), its temperature range (upper limit of 50°C) and its tendency to give erratic and drifting signals.

RESULTS FROM THE ULTRAVIOLET SPECTROSCOPIC WORK

The ultraviolet spectroscopic technique was used as the primary analytical technique for the reasons listed in the Introduction and in the immediately preceding section and because it worked quite well for the pKa determinations.

Spectral Differences:

Figure 9 shows ultraviolet absorption spectra of KC4S solutions (0.00032M) with and without calcium at a pH of about 12.9 at 25°C. Very distinct absorption differences are evident at 240 and at 300 nm. Spectra taken of similar solutions at 80°C are shown in Fig. 10. Two hundred and forty nm was chosen as the analytical wavelength on the basis of these spectra.

No change in the absorption spectrum of KC4S occurred when calcium was added at pH 3, and only a very slight difference was noted at pH 10. This concurs with

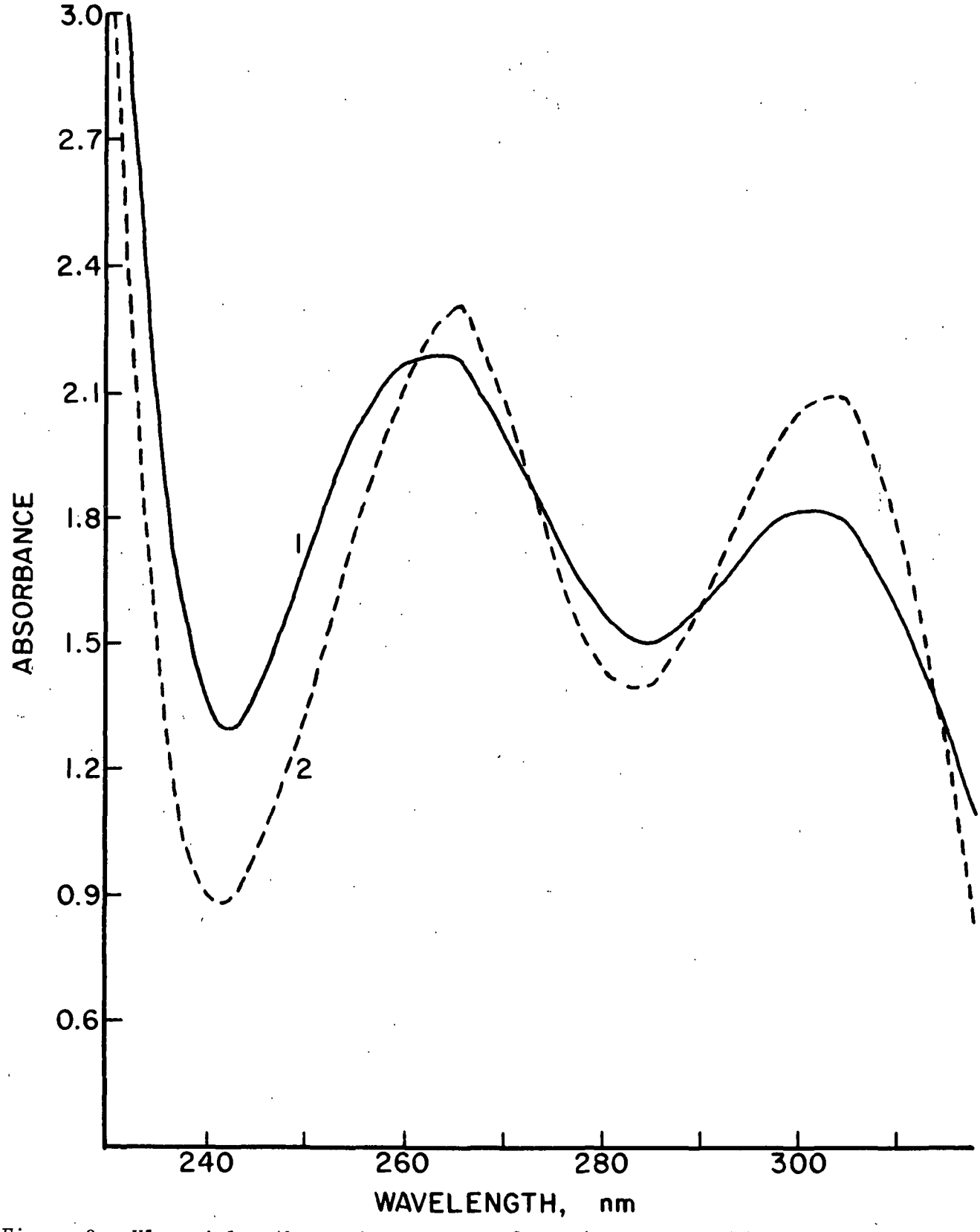

Figure 9. Ultraviolet Absorption Spectra of a KC4S Solution (1) and a Solution Containing KC4S and Calcium (2). (KC4S = 0.00032M, Calcium = 0.00064M, pH = 12.9 for Both Solutions, T = 25°C.)

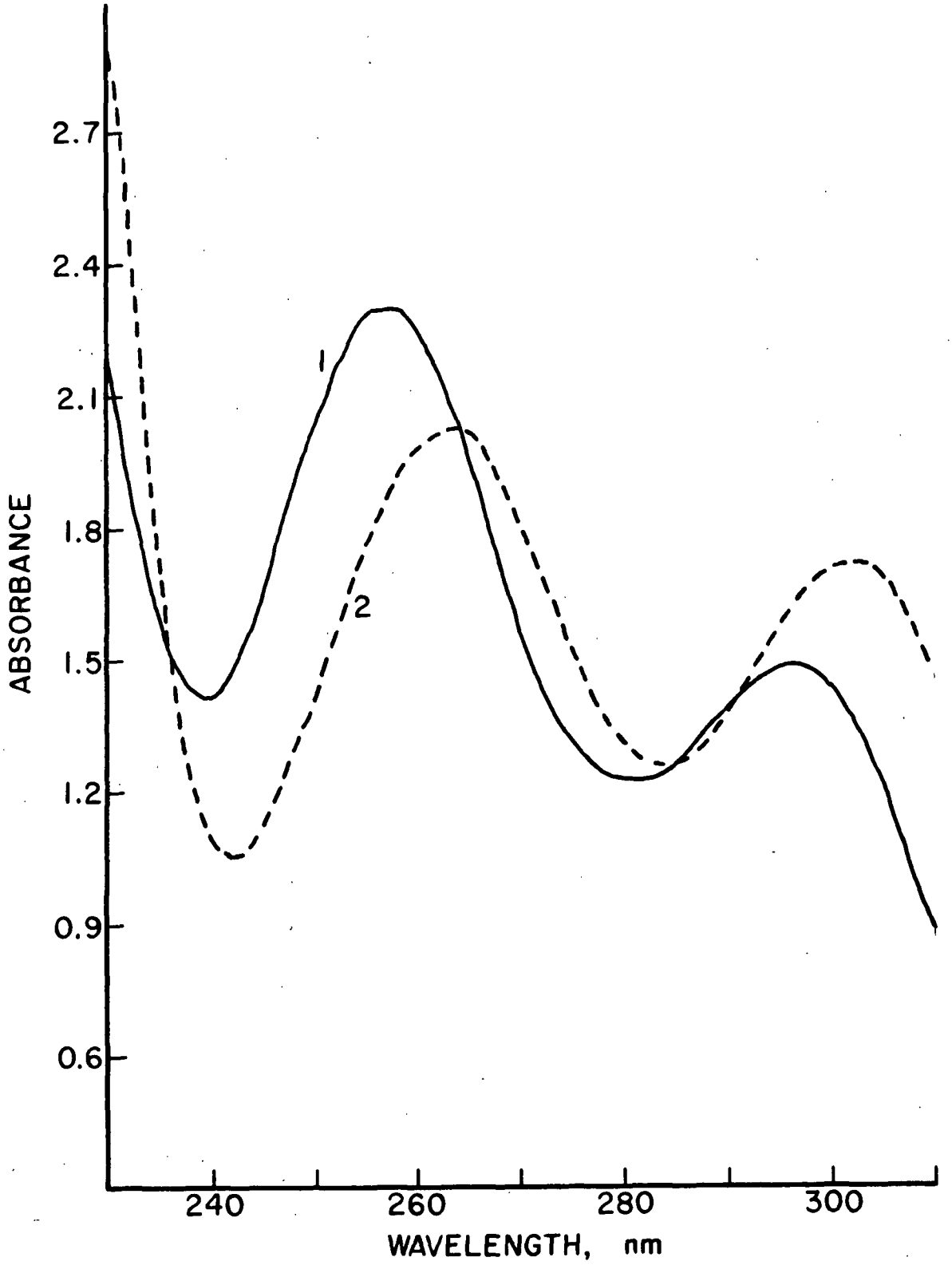

Figure 10. Ultraviolet Absorption Spectra of a KC4S Solution (1) and A Solution Containing KC4S and Calcium (2). (KC4S = 0.00032M, Calcium = 0.00064M, pH = 12.1 for Both Solutions, T = 80°C.)

the results found with the calcium ion selective electrode, which showed that no change in the ionic calcium level occurred when KC4S was added to an acidic or weakly alkaline system.

Stability Constant Values:

The stability constants for the calcium-KC4S complex were determined according to the method described in the Introduction (p. 3) and outlined in the Experimental section. It was found that the experimental data could be explained by assuming that only one complex, with a 1:1 (Ca:KC4S) stoichiometry, existed in the system. The values determined for the logs of the stability constants are shown in Table III.

TABLE III

STABILITY CONSTANTS OF CALCIUM-KC4S COMPLEX
AS DETERMINED UNDER THE CONDITIONS NOTED

Temperature (°C)	Ionic Strength	Log K_{ML}	Log ε_{ML}
5	0.92	3.84	3.38
20	0.92	3.86	3.40
20	0.10	4.64	3.40
40	0.92	3.79	3.40
60	0.92	3.79	3.44
80	0.92	3.80	3.49

Approximate 95% confidence limits* were determined for the log K_{ML} value determined at 20°C and 0.92N ionic strength. This determination was done using the same type of statistical approach employed to determine the confidence limits of the pKa2 values, and is also discussed in the Appendix. The approximate 95%

*See Appendix III.

confidence limits for the stability constant at 20° and 0.92N ionic strength were found to be 3.86 ± 0.15.

The following Fig. (11-15) are plots of the experimental data taken at 5, 20, 40, 60 and 80°C. The dashed lines on each figure indicate where the computed data, which best fit the experimental data, fell when only one complex (of the form Ca_1KC4S_1 with the KC4S being totally dissociated) was assumed to exist in the system.

Possibilities of Other Complex Species:

The approach taken in dealing with this system was to make a minimum of initial assumptions regarding the nature of the interactions which occur between calcium and KC4S. By carefully controlling the experimental conditions, however, the system could be kept reasonably simple. Exclusion of oxygen from the system prevented the occurrence of oxidized forms of KC4S. Also, keeping the pH from getting too high* insured that less than 10% of the calcium in any sample would exist as the monohydroxide (CaOH+).

The analysis of the data was done by first assuming that only the most likely (and also the simplest) forms of the complex existed in the system. The first assumption made was that only one complex, Ca_1KC4S_1 (or ML) formed between calcium and KC4S, and that only the totally dissociated species of the ligand reacted. This assumption gave a good fit to all of the data.

The next step was to try to achieve an even better fit to the data by assuming the existence of additional complex species. Complexes of the form ML_2 and MLH were tried alone and with ML to improve the fit of the calculated data to the experimental data.

*The upper pH limits are discussed in the next section.

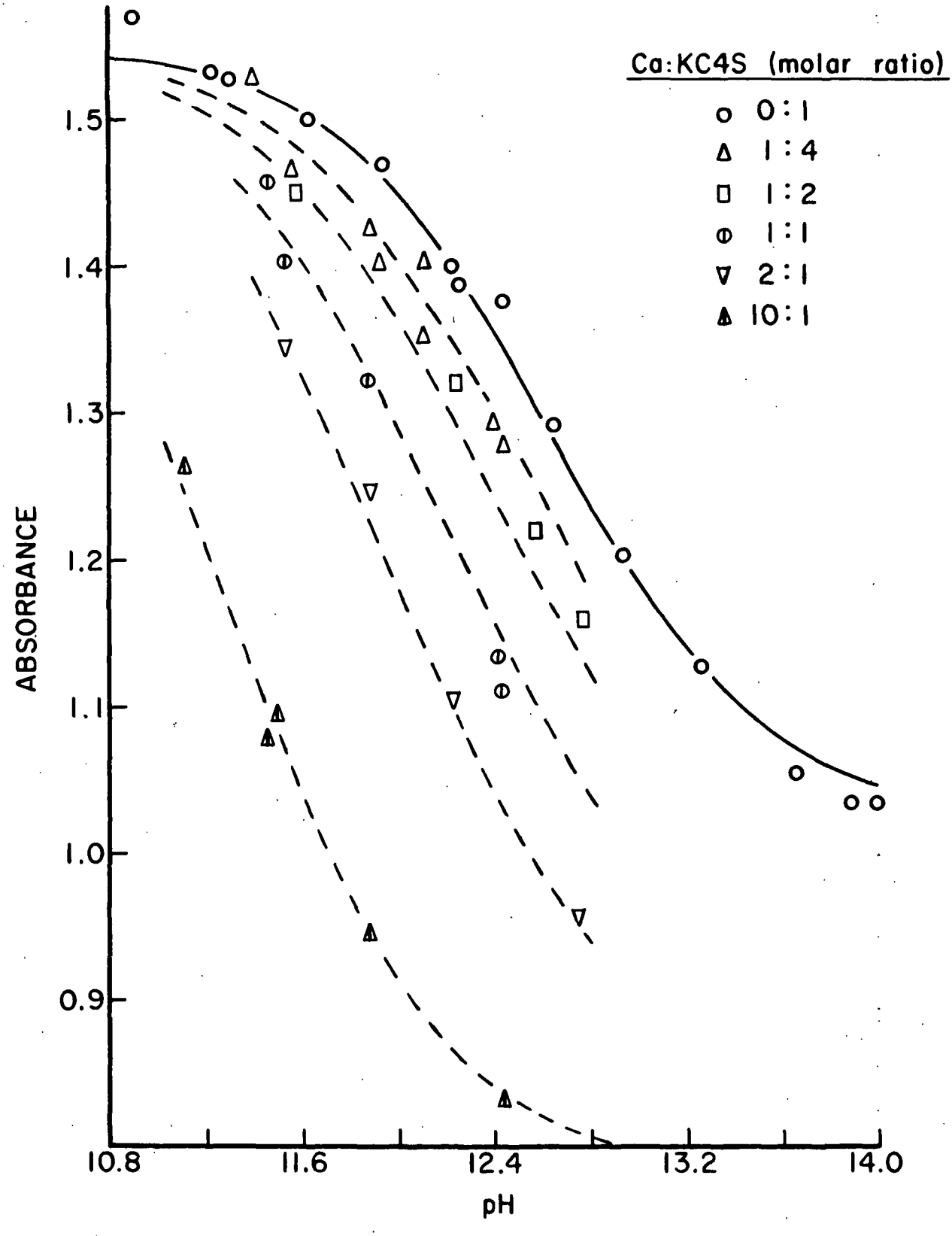

Figure 11. Plot of Experimental Data Points Taken at 5° (0.92N Ionic Strength, 240 nm) and Lines Generated by Computer Program to give the Best Fit to the Data Assuming One Complex, ML Exists. For These Lines, pKa2 = 12.65, log K_{ML} = 3.84 and log ε_{ML} = 3.38

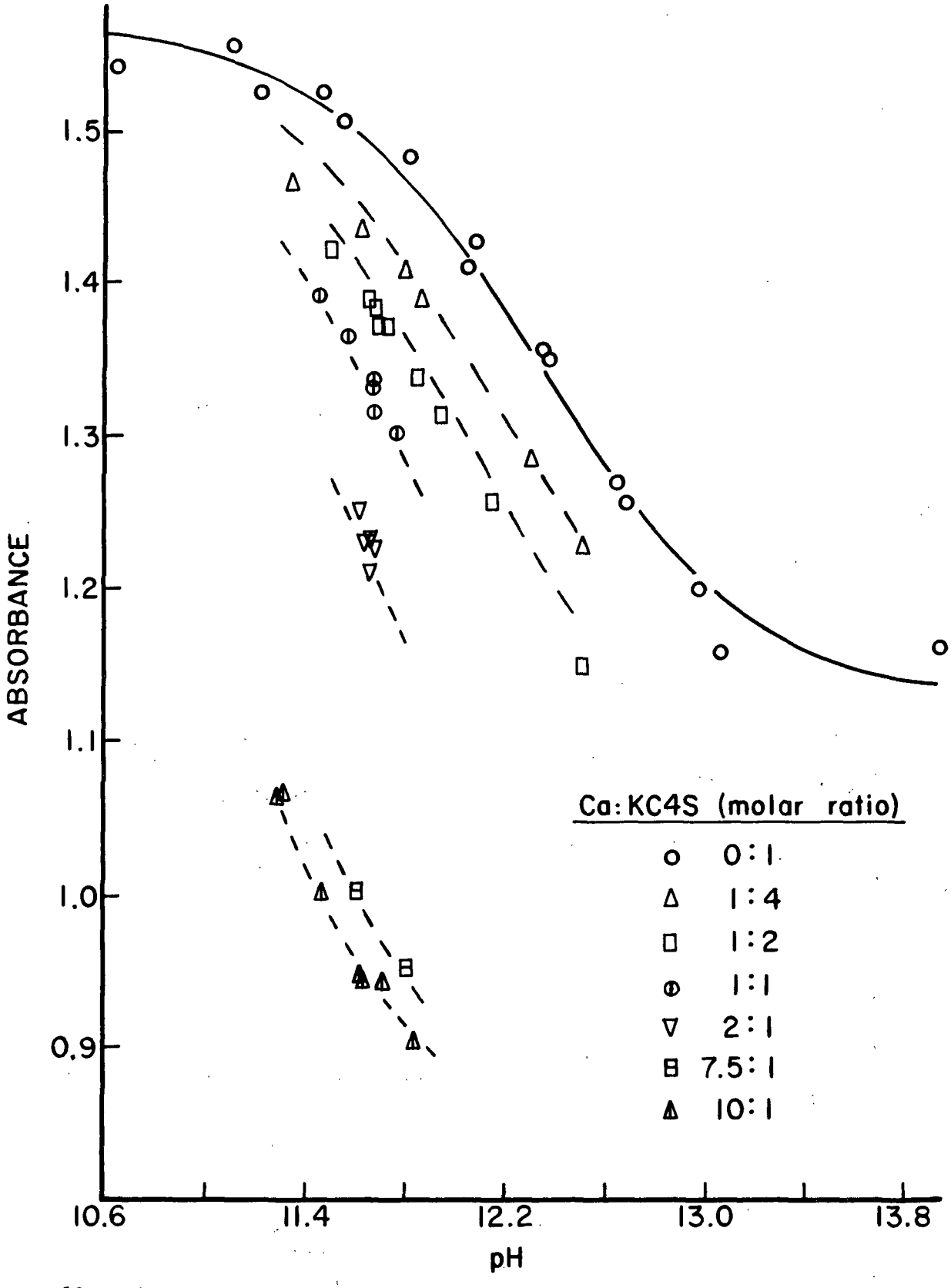

Figure 12. Plot of Experimental Data Points Taken at 20° (0.92N Ionic Strength, 240 nm) and Lines Generated by Computer Program to Give the Best Fit to the Data Assuming One Complex, ML Exists. For These Lines, pKa2 = 12.32, log K_{ML} = 3.86 and log ε_{ML} = 3.40

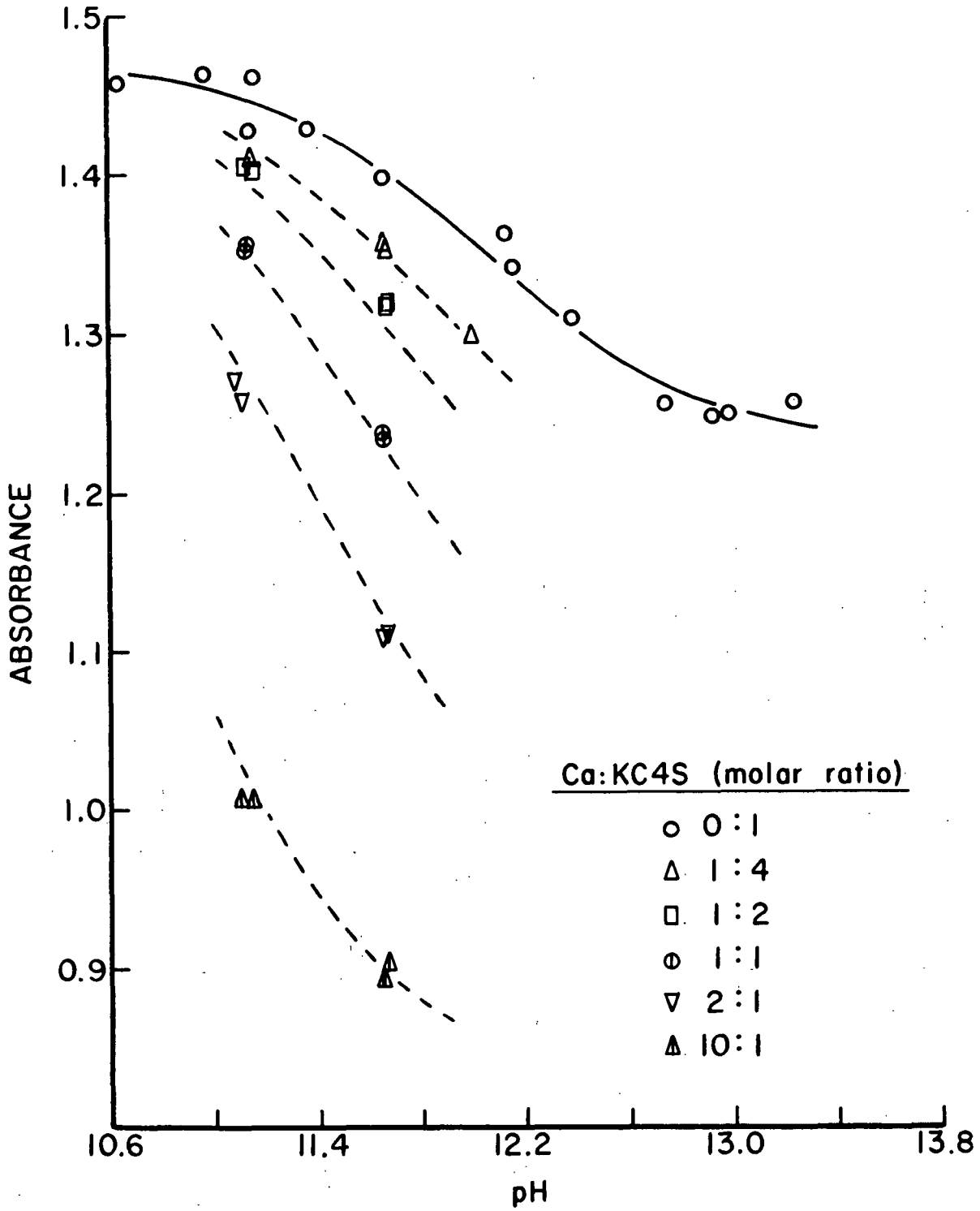

Figure 13. Plot of Experimental Data Points Taken at 40° (0.92N Ionic Strength, 240 nm) and Lines Generated by Computer Program to Give the Best Fit to the Data Assuming One Complex, ML Exists. For These Lines, pKa2 = 12.05, log K_{ML} = 3.79 and log ε_{ML} = 3.40

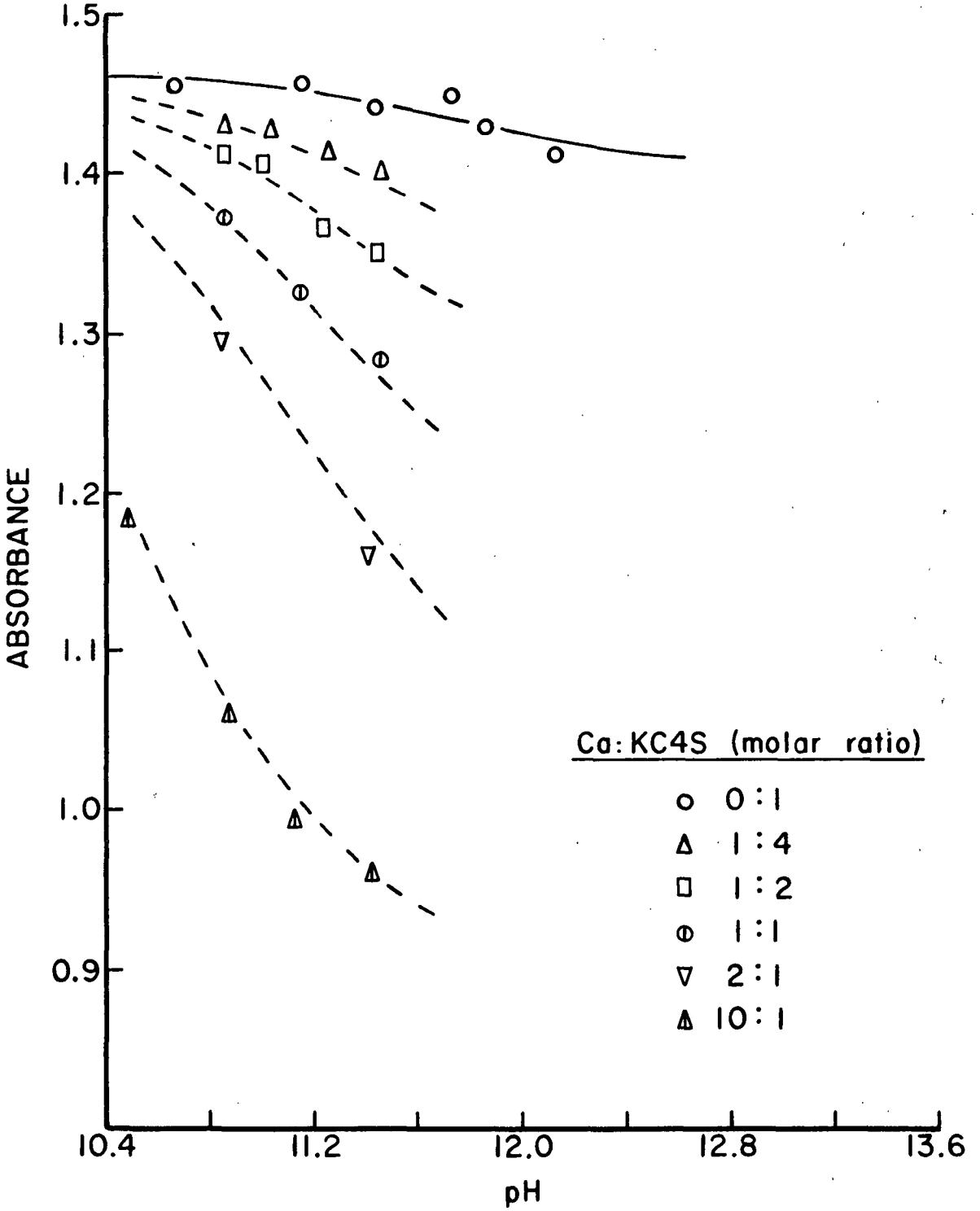

Figure 14. Plot of Experimental Data Points Taken at 60° (0.92N Ionic Strength, 240 nm) and Lines Generated by Computer Program to Give the Best Fit to the Data Assuming One Complex, ML Exists. For These Lines, pKa2 = 11.81, log K_{ML} = 3.79 and log ε_{ML} = 3.44

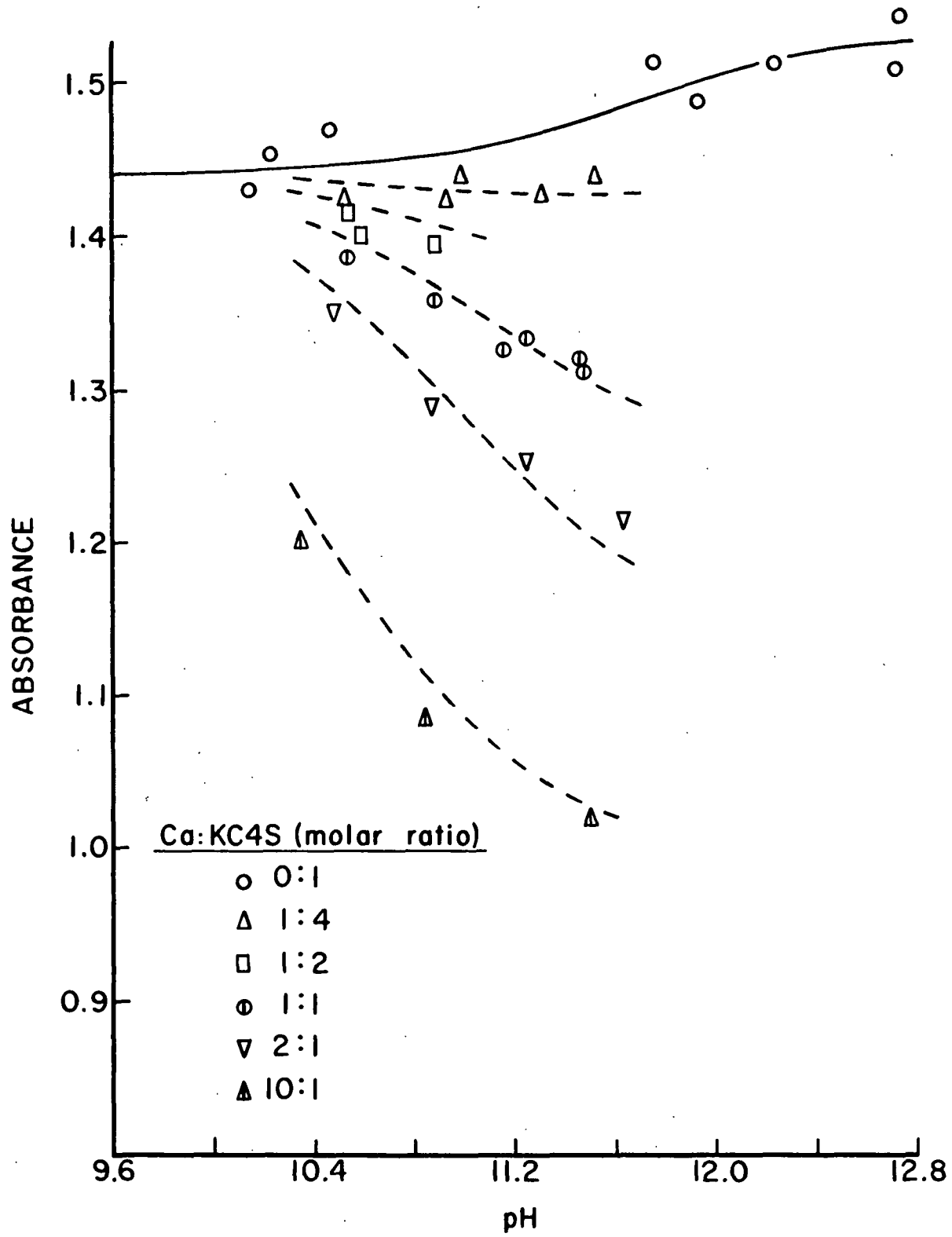

Figure 15. Plot of Experimental Data Points Taken at 80° (0.92N Ionic Strength, 240 nm) and Lines Generated by Computer Program to Give the Best Fit to the Data Assuming One Complex, ML Exists. For These Lines, pKa2 = 11.69, log K_{ML} = 3.80 and log ε_{ML} = 3.49

It was found that a good fit to the experimental data could not be achieved unless ML was assumed to exist in the experimental system. While an improved fit could usually be achieved by assuming the existence of a second complex, ML_2, it was generally found not to be significant. These results are displayed in Table IV.

TABLE IV

FIT OF COMPUTED DATA TO EXPERIMENTAL DATA WHEN ML AND (ML + ML_2) ARE ASSUMED TO EXIST

Temp.	Species Assumed	Log K_{ML}	Log ε_{ML}	Log K_{ML_2}	Log ε_{ML_2}	Fit[a] (S)
5	ML	3.84	3.38	--	--	0.00929
	ML&ML_2	3.83	3.37	2.38	3.90	0.00920
20	ML	3.86	3.40	--	--	0.00611
	ML&ML_2	3.82	3.40	2.77	3.43	0.00473
40	ML	3.79	3.40	--	--	0.00207
	ML&ML_2	3.83	3.40	1.76	4.65	0.00169
60	ML	3.79	3.44	--	--	0.00102
	ML&ML_2	3.79	3.44	0.90	3.52	0.00103
80	ML	3.80	3.49	--	--	0.00460
	ML&ML_2	3.92	3.48	1.69	5.07	0.00101

[a]This fit is the same value described in Equation 12 on page 14. The computer program which was used to calculate these values is contained in Appendix I. Values from one temperature should not be compared directly to those at another as different numbers of samples were used for each temperature (50-26 samples, 20°-35, 40°-20, 60°-17, and 80°-21).

A statistical F-test was employed to indicate the significance of the improvement in fit that was offered by the second complex. The results from this test indicate that at 20, 40, 60 and 80°C, the discrepancy between the experimental data

and the "data" calculated by assuming one complex, ML, can be explained on the basis of experimental error. At 5°, while the fit based on a single complex was not as good (Table IV), the improvement in fit achieved by assuming a second complex is negligible. An example of how the F-test was used can be found in Appendix IV, for the data taken at 20°C.

The experimental data can be explained on the basis of a single, stable complex of the form ML. The possibility of a second, much less stable complex of the form ML_2 can neither be substantiated nor rejected on the basis of these experimental data. However, if a second complex of the ML_2 form does exist, it is much less stable than the ML form (on the average, $K_{ML_2}:K_{ML} = 3:100$), and of minor importance in predicting the amount of free calcium in the experimental system.

The Possibility of Interference from $CaOH^+$

The log of the equilibrium constant associated with the formation of $CaOH^+$ was reported by Olin (28) to be 0.642 at 25° and at an ionic strength of approximately 3M ($NaClO_4$). From these values, it can be estimated that at 25°, and at pH 12, less than 5% of the calcium in an aqueous solution would exist as $CaOH^+$ and at pH 13, about 25%.

The data point with the highest pH at 20° in this study in a system containing calcium was about 12.5. The data points taken at the other temperature were kept in a similar range (relative to the pKw). The fact that no pH effect was observed in the calculated fit to the data gave additional reason to discount the possibility of any significant effect being exerted on the system by the possible existence of the calcium monohydroxide.

RESULTS ACHIEVED WITH THE CALCIUM ELECTRODE

The calcium electrode was used to verify the results of the ultraviolet work. It was used as the back-up analytical technique rather than the primary analytical technique for the reasons noted on page 31. Only minimal drifting problems were encountered under the conditions the electrode was used (pH 10 to 11, room temperature).

The approach taken in using the electrode was to mix solutions of known calcium and ligand concentrations at an ionic strength of 0.1N (KCl). The temperature was noted and the pH of the solutions measured. The ionic calcium level was then predicted, based on the stability constant of the complex and the pKa_2 of KC4S which had been determined at 0.1N ionic strength and 20°C using the ultraviolet technique. The predicted ionic calcium was then compared to the ionic calcium level measured with the calcium electrode. The results are shown in Table V.

The ionic calcium measurements were also used as the basis for an independent determination of the stability constant of the ML complex. The average log K_{ML} value determined from these measurements was 4.65 as compared to 4.64 from the UV method.

The good agreement between the measured ionic calcium levels and those predicted on the basis of one complex (Table V) are further evidence that the effect of KC4S on calcium distribution in the experimental system can be accurately predicted on the basis of a single complex species, ML. This was true even when the system was swamped with ligand (which would favor formation of ML_2).

TABLE V

COMPARISON OF IONIC CALCIUM LEVELS MEASURED WITH THE CALCIUM ELECTRODE AND PREDICTED BASED ON THE RESULTS FROM THE ULTRAVIOLET DETERMINATIONS

Sample Solution	KC4S:Ca^{++} (Mole:Mole)	pH	Measured Ca^{++} (ppm)	Predicted Ca^{++} (ppm)
1	4:1	10.80	20.7	21.8
2	8:1	10.91	8.7	9.0
3	10:1	11.36	2.2	2.7
4	4:1	10.60	31.2	29.9
5	8:1	10.33	25.6	26.6
6	10:1	10.07	30.2	34.1
7	2:1	10.14	71.2	70.7
8	4:1	10.48	36.4	36.0
9	6:1	10.42	28.3	28.9
10	1:1	10.29	78.8	79.3
11	2:1	10.72	43.4	44.2
12	4:1	10.51	33.4	35.4

COMPARISON TO MURAKAMI'S RESULTS

Only one earlier worker, Murakami (15), has attempted to determine a stability constant for the calcium-KC4S complex. He carried out his work in dilute (0.1N KNO_3) aqueous, alkaline systems at 30°C. He reported that two complexes formed, Ca_1KC4S_1 and Ca_1KC4S_2 (or ML and ML_2), and that only the totally dissociated KC4S complexed.

Several aspects of the analytical technique employed by Murakami are subject to question. The first is that his data were taken at a relatively low pH (<11) although only the totally dissociated form of KC4S complexed. Secondly, the potentiometric titration procedure which he employed was used to determine stability

constants based on pH differences of systems containing KC4S with and without calcium. As is evident from Fig. 16, the differences between the KC4S curve and the KC4S plus calcium curve are very small. Finally, the fact that the KC4S plus calcium line is dotted indicates that Murakami found it to be "nonequilibrated," which indicates that the conditions were suspect for making a determination of an equilibrium constant.

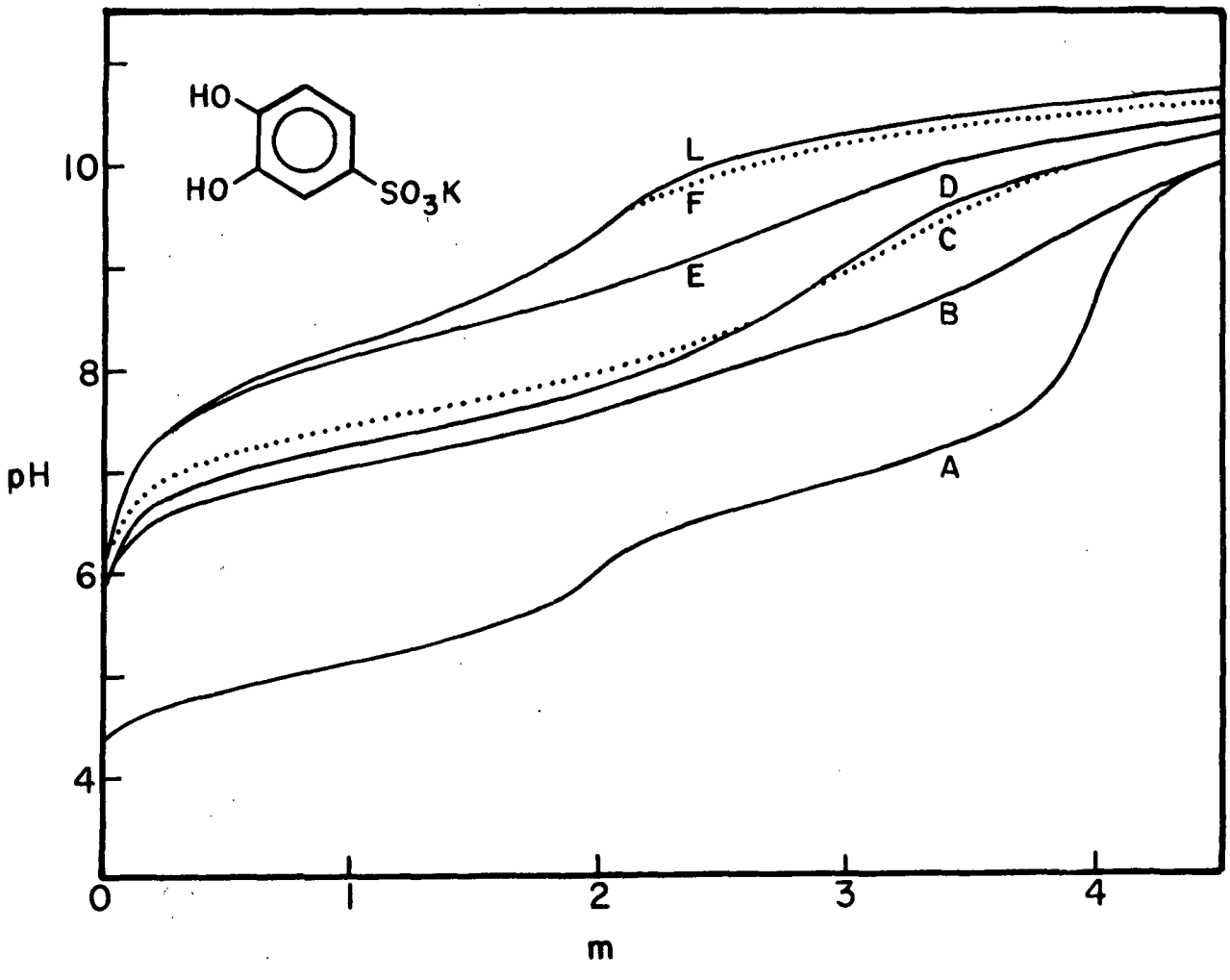

Figure 16. From Murakami (15). Potentiometric Titration Curve of KC4S Plus Several Transition and Alkaline Earth Metals*. F = Calcium (m = Moles of Base per Gram Ion of Metal; Reaction Conditions; 30°C, 0.1N KNO_3 and Metal Concentration = 5.00×10^{-4}M)

*A,Cu;B,Zn:C,Co;D,Ni;E,Mg.

THERMODYNAMICS OF THE COMPLEX FORMATION

As with the pKa_2 (page 28), a linear regression analysis of ln K_{ML} vs. 1/T will yield a line of slope $-\Delta H_{0.92}/R$. Such an analysis was done on the data in Table III (page 34), and the heat of reaction ($\Delta H_{0.92}$) for the complex formation at 0.92N ionic strength was determined to be:

$$\Delta H_{0.92} = 8.314 \frac{\text{Joules}}{^\circ\text{K mole}} \times -185^\circ\text{K} = -1{,}540 \text{ Joules/mole} \qquad (25).$$

The negative value for $\Delta H_{0.92}$ indicates that the reaction is exothermic, which is usual for a bond forming reaction (38). The negative $\Delta H_{0.92}$ value also reflects the slight decrease in K_{ML} with temperature, and predicts that ionic calcium will be released as temperature is increased because of this.

The free energy and entropy changes associated with the formation of the complex were calculated at each experimental temperature from Eq. (23) and (24), respectively, shown on pages 29 and 30. The results from these calculations are shown in Table VI.

TABLE VI

THERMODYNAMIC QUANTITIES ASSOCIATED WITH THE FORMATION OF THE CALCIUM-KC4S COMPLEX

Temperature	$\Delta G_{0.92}$(KJ/mole)	$\Delta S_{0.92}$(J/mole °K)
5	-20.5	68
20	-21.7	69
40	-22.7	68
60	-24.2	68
80	-25.7	68

Bond forming reactions typically have negative heats of reaction and negative entropy changes (38). The positive change in entropy which occurs is likely due to the release of coordinated water molecules from the calcium as it reacts with KC4S, as shown in Eq. (26).

$$KC4S + Ca\cdot(H_2O)_6 \rightleftharpoons (H_2O)_4\cdot CaKC4S + 2H_2O \qquad (26)$$

As with the pKa_2, the consistency of the ΔS values can be attributed to the relative independence of ΔH to temperature in the 5° to 80°C range (38).

The free energy changes associated with the formation of the complex which are shown in Table VI are, again, consequences of Eq. (24) ($\Delta G = \Delta H - T\Delta S$). As ΔH and ΔS are constant, as T increases, ΔG must decrease.

When considering these thermodynamic values it is important to realize that the effect of temperature (from 5° to 80°C) on the stability constant values was less than the estimated error associated with the values themselves. Consequently, there is a large degree of uncertainty associated with all of the reported thermodynamic values for the formation of the complex. The values are reported here strictly as a matter of record.

EFFECT OF KC4S ON CALCIUM DISTRIBUTION

The primary purpose of this thesis is to predict the effect that KC4S has on ionic calcium concentration. The effect of KC4S on the distribution of ionic calcium in an aqueous, alkaline system is shown using a three dimensional plot in Fig. 17. This particular plot corresponds to data taken at a calcium:ligand molar ratio of 1:2. Plots for each of the other molar ratios (1:4, 1:1, 2:1 and 10:1) are very similar to Fig. 17 and are contained in the Appendix.

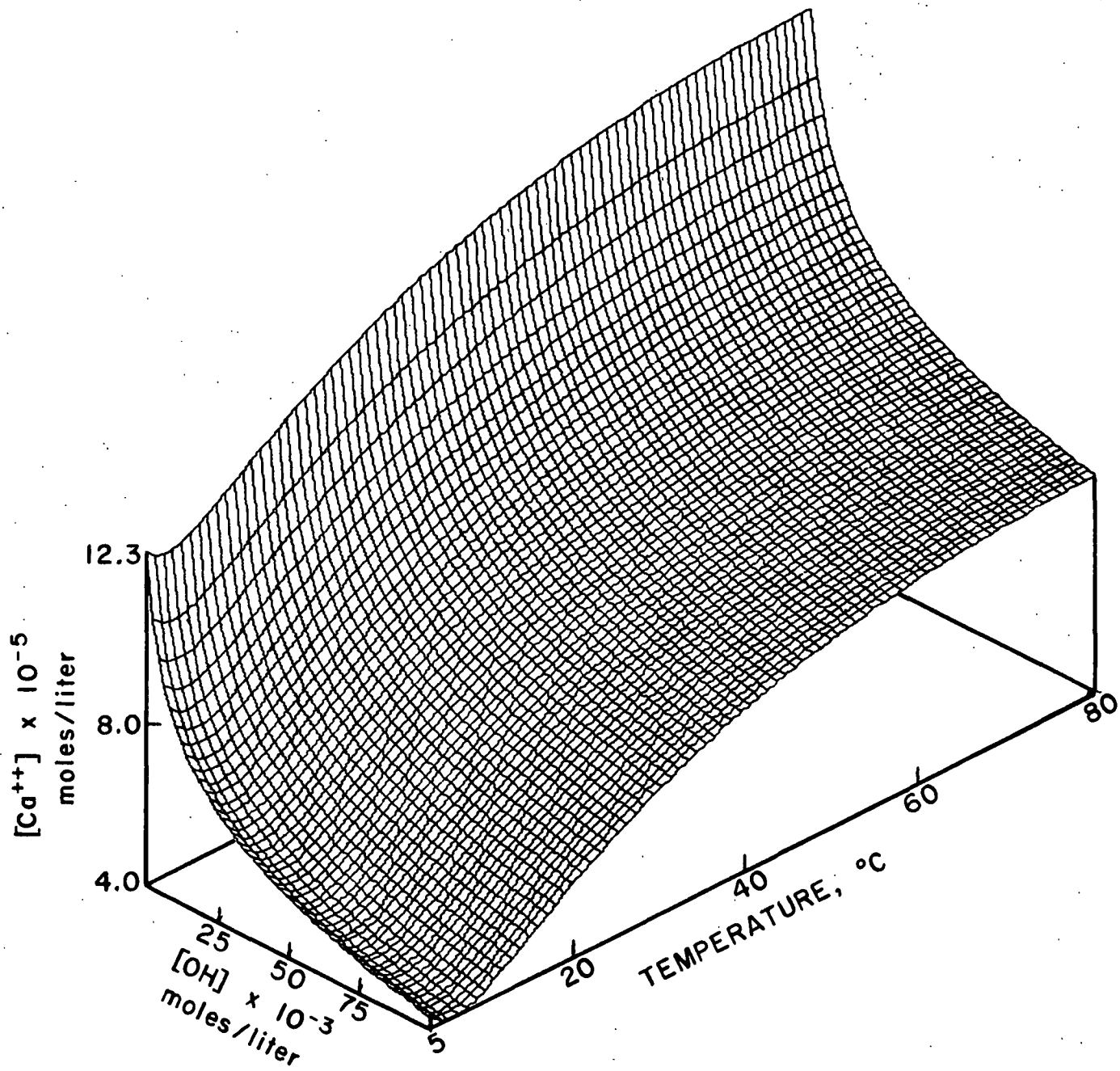

Figure 17. Variation of Ionic Calcium with Base Concentration and Temperature. [0.92N Ionic Strength (KCl), Molar Ratio of Calcium:KC4S of 1:2]

SIGNIFICANCE OF THE PLOT

In Fig. 17, the ionic calcium level is seen to fall off dramatically as the base concentration (pH) is increased. This is due to increased formation of the complex, which is in turn due to the shift of KC4S from the partially dissociated form to the reactive totally dissociated form.

The increase in the level of ionic calcium that occurs with increases in temperature is caused by a decrease in the amount of complex that exists. This is primarily due to the lowering of pH that occurs when an alkaline, aqueous solution is heated. The pH lowering is brought about by the lowering of pKw that occurs as temperature is increased (Table VII). This decrease in the pH causes a shift from the reactive totally dissociated form of KC4S to the nonreactive partially dissociated form.

TABLE VII

ION PRODUCT K_W OF WATER FROM 0 TO 60° (35)

T °C	$K_W \times 10^{14}$	$-\text{Log } K_W$
0	0.1139	14.943
5	0.1846	14.734
10	0.2920	14.535
15	0.4505	14.346
20	0.6809	14.167
25	1.008	13.996
30	1.469	13.833
35	2.089	13.680
40	2.919	13.535
45	4.018	13.396
50	5.474	13.262
55	7.297	13.137
60	9.614	13.017

When attempting to relate the results found in this study to those found by Frederick and Grace one must realize that their work was conducted at higher temperatures (up to 150°C). Still, the results of the present study which show an increase in the ionic calcium concentration at higher temperatures supports Frederick and Grace's hypothesis that heating the complex causes it to dissociate. The dissociation was not found to be due to a change in the stability constant of the complex as predicted, however, but rather to the change in pKw that occurs with temperature change.

METHOD OF DATA PROJECTION

The data from the experimental solutions of each of the five calcium to ligand ratios that were used in determining the stability constants of the complex were grouped together.* Each of these samples contained a carefully measured amount of base (potassium hydroxide) and was analyzed at a known temperature (5, 20, 40, 60 and 80 degrees). Later, once the stability constants and the acid dissociation constants were known at each temperature, the ionic calcium concentration of each sample was computed. (The accuracy of these computed values has been demonstrated with the calcium electrode.) For each original sample, then, three coordinate points, temperature, base concentration, and ionic calcium concentration, were produced. Approximately 25 points were used to determine each surface. The surfaces themselves were generated using a multiple regression program and offer a very close fit to the actual data.

*Recall that originally (Fig. 11-15) the experimental solutions were grouped together by temperature so that the K_{ML} value at each temperature could be determined.

CONCLUSIONS

The totally dissociated form of the potassium salt of catechol-4-sulfonate (KC4S) formed a stable complex with a 1:1 stoichiometric ratio with calcium. The stability constant of the complex showed no strong dependence on temperature, and its log was determined to be 3.82 ± 0.04 in the temperature range of 5 to 80°C. All of the experimental data that were gathered at 0.1N and 0.92N ionic strength, from 5 to 80°C and at Ca:KC4S molar ratios ranging from 10:1 to 1:10 could be explained on the basis of the existence of the single complex species.

Although the stability constant of the complex was found to be essentially independent of temperature from 5 to 80°C, the net effect of heating a solution containing the complex was to increase the amount of ionic, or scalable calcium. This is because of the pH drop which occurs upon heating an aqueous, alkaline solution, which causes a shifting of the ligand from its reactive, totally dissociated form to the inactive, partially dissociated form. The drop in pH is a result of the inverse relationship between the pKw and temperature.

This thesis work lends support to the hypothesis of Frederick and Grace that lignin fragments in spent alkaline pulping liquor can play an integral role in the calcium carbonate scaling mechanism by complexing with ionic calcium. It suggests, however, that the dissociation of the complex and the release of the scalable calcium is not due to a weakening of the complex at higher temperatures, but rather to an equilibrium shift involving the free ligand which stems from a pH change that occurs with heating.

EXPERIMENTAL

MODEL COMPOUND SYNTHESIS

PROCEDURE

The potassium salt of catechol-4-sulfonate was synthesized according to the method outlined by Ray and Dey (48). While the synthesis itself is straightforward, the purification of the model compound was a rather tedious procedure. As the description of the synthesis given by Ray and Dey is very brief, it will be discussed here in a little more detail.

Four separate reactions were run in order to get the needed amount of KC4S. In each, 500 grams of reagent grade catechol and a slight molar excess (about 270 mL) of concentrated sulfuric acid (H_2SO_4) (d. 1.84) were combined together with several small pieces of iodine in a 1000 mL beaker. The beaker was placed in an oil bath at 50-55°C and left there for 1-1/2-2 hours. Stirring was done with a Teflon magnetic stirring bar.

The reaction was then allowed to cool before the viscous slurry was added to 1500-2000 mL of triply distilled water. The resulting solution was clear, with an amber color.

Barium hydroxide was added to remove the excess sulfuric acid. The barium sulfate was filtered off through celite. Just enough sulfuric acid was added to the solution to remove the barium. This was accomplished by adding H_2SO_4 until no more barium sulfate precipitated. (This was done in several steps.) Finally, potassium hydroxide was added to the filtrate until the pH was 7.00 ± 0.01. The liquor was then concentrated and the crystals removed. Recrystallization from triply distilled water was done until the needle-shaped crystals were bright white.

This involved as many as five separate recrystallizations. The reaction sequence is shown in Fig. 18.

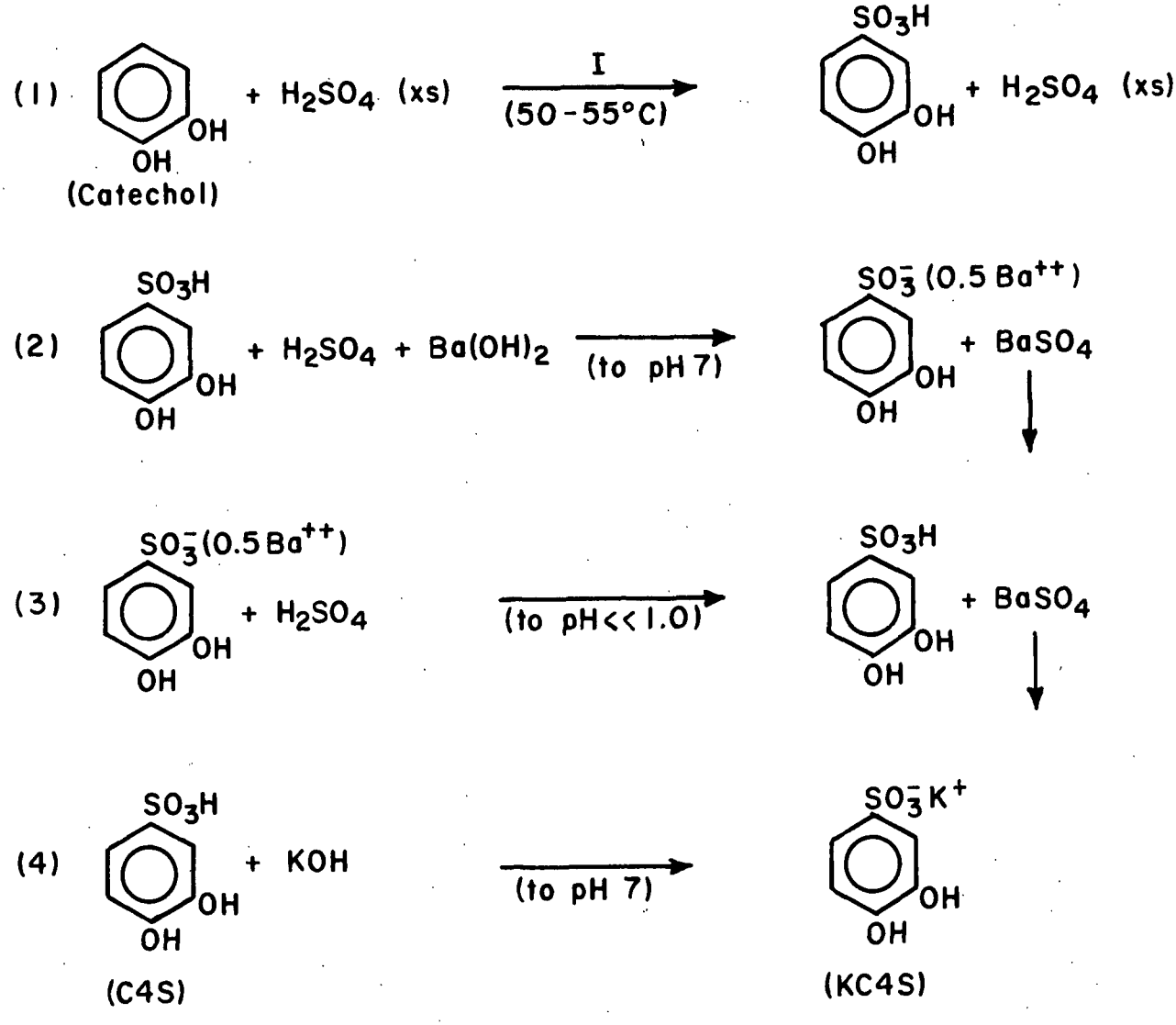

Figure 18. Synthetic Route for Making Potassium Catechol-4-Sulfonate (KC4S) from Catechol

Several brands of decolorizing carbon were used in an attempt to remove the color from the liquor to no avail. Also, extractions with various organic solvents were tried on one or two mL samples of the liquor without success. It was found that the color problem could be reduced by recrystallizing the catechol from water prior to using it in the reaction.

CONFIRMATION OF PRODUCT PURITY

Elemental Analyses:

Samples of the synthesized KC4S were sent to two private firms which specialize in performing elemental analyses of compounds. In addition, some analytical work was performed at the Institute. The results from these analyses are shown in Table VIII.

These results indicate that a compound with a chemical formula of $C_6H_5O_5SK$ was successfully synthesized.

TABLE VIII

ELEMENTAL ANALYSES OF THE MODEL COMPOUND

	% C	% H	% O	% S	% K
Theoretical[a]	31.57	2.21	35.04	14.05	17.13
Chemalytics	32.01	2.36	--	13.87	--
Micro-Tech (1)	31.43	2.11	--	13.86	--
(2)	31.34	2.15	--	13.85	--
IPC Analytical Group (1)	--	--	--	(15.6)	17.0
(2)	--	--	--	(16.1)	17.2
Average	31.59	2.21	35.2	13.86	17.1

[a]Based on $C_6H_5O_5SK$. Numbers in parentheses were not figured in the averages.

NMR Spectra:

Both carbon and proton NMR spectra were taken of the model compound. The results of these spectra indicate that the sulfonate group is located at the 4 position on the aromatic ring. A detailed analysis of the spectra is included in the Appendix.

Melting Point:

The melting point of KC4S was determined to be 306-308°C. No values for this melting point are reported in the literature.

Trace Elements:

As a precaution, the synthesized KC4S was checked for metal contaminants. The results indicated trace amounts were present but in insignificant quantities (Fe = 70 ppm, Al = 23 ppm, Cu = 17 ppm, Ba, Pb, Ca, and Zn not detected).

SPECTROSCOPIC METHOD

SAMPLE PREPARATION

Chemicals:

All of the chemicals used to prepare the samples were of reagent grade quality or better. Concentrated solutions of reagent grade potassium hydroxide (KOH) which were free of carbon dioxide (Acculute) were diluted to obtain 1N KOH solutions.

The potassium nitrate (KNO_3) which was used in some of the preliminary work as an ionic strength adjuster, and the calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) used throughout the study were reagent grade. The potassium chloride (KCl) used was of a very high purity (Alfa Ultrapure). The ultrapure KCl was used as a precaution because of the relatively large amounts of it which were needed to maintain an ionic strength of 0.92N.

Water:

The water used to prepare all of the standard and sample solutions was triply distilled (3D), the second distillation from alkaline permanganate. Deionized, distilled water (1D) from a commercial still was redistilled from a solution of 0.02% $KMnO_4$ and 0.05% KOH (w/w) to remove any organic impurities. It was then distilled

a third time from a pot containing no additives. The conductivity of the 3D water was checked regularly to insure it stayed below 2.0×10^{-6} ohm^{-1} cm^{-1}.

Glassware:

All of the glassware used to prepare or store the samples or standard solutions from which the samples were prepared was thoroughly cleaned prior to use. This involved first degreasing the glassware by washing it with alconox. The glassware was then soaked in 1N KOH, rinsed and soaked in 1N nitric acid (HNO_3), followed by treatment in a dilute KOH solution and a dilute HNO_3 solution. Finally, the glassware was thoroughly rinsed, first with 1D and then with 3D water. Once the data taking process was begun, the glassware was only contacted with sample solutions and 1D or 3D water. All of the sample glassware was rinsed repeatedly between runs.

Procedure:

The samples which were prepared for analysis with the ultraviolet spectrometer were all prepared in the same manner, whether they were to be used to determine the pKa2 of KC4S or the stability constant of the calcium-KC4S complex. Between eight and twelve samples were prepared and analyzed together.

The samples were prepared in 50 mL volumetric flasks which were contained in a nitrogen atmosphere. This preparation was done volumetrically using standard solutions which had been prepared in nitrogen from freshly boiled 3D water and also stored under nitrogen. The standard solutions from which the samples were prepared were: KOH, 1N; KCl, 1N; KC4S, 0.008M; $CaCl_2 \cdot 2H_2O$, 0.08M and triply distilled water. The KC4S, $CaCl_2 \cdot 2H_2O$ and 3D water were added to the sample flasks using an adjustable pipette (Finnpipette) which was tested and found to accurately deliver within 1% the amount of solution required between 1 and 5 mL. The potassium hydroxide was added using a 1.0 mL glass syringe, and the samples were diluted to volume using

1.0N KCl. The total volume of KOH + KCl added to each sample was always 46 mL, so that the ionic strength of each sample was 0.92N. When lesser amounts of calcium were required, a small aliquot of the calcium standard solution was diluted to the required strength.

A blank solution was also prepared which contained KCl and KOH. It was found that as neither species exhibited significant absorption in the 220 nm to 300 nm range it was not critical how much of each species was present. However, the blank was always prepared so that it had an ionic strength of 0.92N and a pH similar to that of the samples. As a precaution, the blanks were also prepared under nitrogen in the manner that the samples were.

The nitrogen atmosphere in which the samples were prepared was contained in a glove bag from which all of the air had been removed by using a vacuum to pull the bag as flat as possible. This was done several times. Each time the bag was refilled with prepurified nitrogen. The empty sample flasks were all thoroughly flushed with nitrogen prior to being placed in the bag. If even a small amount of oxygen were allowed to penetrate the bag, the samples would take on a yellow color within several minutes and the run would have to be done over.

ANALYSIS OF SAMPLES

Sample Handling:

As soon as a sample was prepared, the 50 mL volumetric in which it was contained was tightly stoppered and it was placed in a small desiccator within the glove bag. After the last sample was placed in the desiccator it was sealed, removed from the glove bag and carried to a second glove bag near the Perkin Elmer (Model 576) spectrometer, where it was once again enclosed in a nitrogen atmosphere.

The samples were analyzed using Beckman matched quartz cuvettes that were fitted with Teflon stoppers. The cuvettes were filled and sealed within the bag. Once the instrument had been calibrated and zeroed (using either 3D water or the blank solution) the samples were analyzed. Each sample was placed in the sample holder and allowed to reach temperature (6-10) minutes before a reading was taken. Readings were only taken when the instrument registered a stable reading for at least 30 seconds.

The unused portions of the sample solutions were kept sealed under nitrogen until all of the spectroscopic work was completed. The pH of each sample was then measured. To accomplish this, the samples were transferred to 25 mL Erlenmeyer flasks (with ground glass stoppers) which were immediately placed in a temperature bath. The pH of each sample was measured while it was in the bath. The samples were then discarded.

pH Measurements:

pH Measurements above 11 must be made with great care to prevent experimental error. Two of the most common causes of experimental error in high pH measurements are caused by the alkaline error* and by inadequate calibration of the electrode (27).

The first problem was overcome with the use of a high pH electrode (Beckman Model No. 39501) and by using potassium as the alkaline cation rather than sodium. The manufacturer claims an alkaline error of less than 0.01 pH unit at pH 13 in KOH (49). Readings taken in high pH solutions used in this study with the 39501 electrode were found to be consistent and stable.

*Alkaline error is caused by an increase in the porosity of the glass to cations not present in the glass. Sodium ions are worse offenders than lithium, and potassium ions are the least offensive of the three (32).

To insure the correct calibration of the electrode, a high pH standard solution was prepared according to NBS methods as outlined by Bates (32). The standard solution was prepared fresh every six months using 3D water and calcium hydroxide prepared by burning reagent grade calcium carbonate (at 1000°C for 1 1/2 hours) to calcium oxide and then slaking it. It was regularly checked by titration with 0.1N hydrochloric acid using a phenolphthalein indicator. A commercial buffer of pH 10.00 was used for the lower pH standard.

For the data taken at 80°C it was necessary to use standard buffers of pH 7.00 and 10.00. However, the pH of the samples was lower at 80° (as the pKa2 of KC4S is lower) and it was found that this particular electrode's slope was relatively consistent over large pH spans.

The pH meter used throughout this study was the Orion Model 901 Ionalyzer. Its attractive features include its high precision, its adjustable slope, its flexible output modes (readings can be taken as pH, millivolts or parts per million among others) and its liquid crystal display. Its performance was tested every several months according to the method outlined in the users manual.

EXPERIMENTS WITH THE CALCIUM ELECTRODE

The calcium ion-selective electrode was used only in a very simple capacity in this study. Its use involved calibrating it in solutions of known ionic calcium concentration and then measuring a solution of intermediate, but unknown, calcium concentration. As noted earlier, the electrode's response was less than ideal, as its readings drifted and it behaved erratically under some conditions, particularly at higher temperatures.

The experiments that were done to check the stability constant values which had been determined using the ultraviolet spectroscopic technique were carried out at

room temperature (about 22°C) in open beakers set on magnetic stirrers. The exact procedure followed in these experiments is outlined in the following steps.

1. Two standard 0.1N KCl solutions were prepared (in air). Solution A contained 100 ppm calcium while Solution B contained 10 ppm calcium. Approximately 1.0 mL of 1.0N KOH was added to each solution.

2. 100 mL of Solution A was added to each of four 250 mL beakers, while 100 mL of Solution B was added to a fifth beaker. A 2 inch Teflon stirring bar was placed in each beaker and turned slowly.

3. Beakers No. 1 and 5 were set aside to calibrate the electrode. To each of the remaining three beakers (which contained 100 ppm calcium solution) different amounts of KC4S were added to establish a KC4S to calcium ratio of from 1:1 to 10:1 (mole:mole).

4. KOH was added to each of the three beakers containing KC4S until the pH was between 10 and 11. The pH was recorded.

5. The calcium electrode was calibrated using Solutions no. 1 and 5, and then dipped in each of the remaining three beakers for several moments until a semi-stable reading was obtained.

6. These measured ionic calcium values were then compared to ionic calcium values which had been computed using the simple mass balance and equilibrium equations, and the values for pKa2 and K_{ML} determined from the ultraviolet spectroscopic work.

NUMERICAL ANALYSIS

As noted in the Introduction, the stability constant and the structure of the calcium-KC4S complex were determined from a "best fit" solution to a series of equations. This was accomplished in the following manner.

1. Certain complex species were assumed to exist in the system.

2. Initial values for the stability constants and the molar absorptivities of the assumed complex species were assigned.

3. Appropriate mass balance and equilibrium constant equations were formulated and inserted into the computer program (contained in Appendix I).

4. The computer was then used to calculate a "data set" based on the initial assumption and using the assigned values for the stability constants and molar absorptivities.

5. These "data" were compared to actual experimental data.

6. The computer program would then cause the values for the stability constants and the molar absorptivities to be adjusted slightly so as to achieve a better least squares fit between the calculated data and the experimental data.

7. When the computed data fit the experimental data as closely as possible, the calculations were terminated and the values for the logs of the stability constants and the molar absorptivities of the proposed complex species which gave the best fit to the experimental data were printed.

8. A new assumption regarding the species of complex which exist in the system would be made and the process would be repeated.

ACKNOWLEDGMENTS

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APPENDIX I

COMPUTER PROGRAM FOR DETERMINING STABILITY CONSTANTS

The stability constants of the calcium-KC4S complex were determined with a program that calculates a "best fit" solution for a function of several variables. The program is comprised of six subroutines which are shown, along with a brief explanation of what they do, in Fig. 19. It is stored in two parts under PLODR1 and PLODR2 (HHW).

The program relies on data from two external sources. For the listing that follows they are TEMP20 (on disk file) and DATA20 (in library). TEMP20 provides the quantities TM (total metal concentration of each sample), TL (total ligand concentration) and S ($\{H\}/K_{HL}$) while DATA20 provides the absorption measurement for each sample (ABSB).

Prior to using the program, an assumption must be made regarding the complex species which are thought to exist in the experimental system. On the basis of this assumption, appropriate mass balance and equilibrium constant equations and their negative partial derivatives are inserted into subroutine UPDATE. Initial values for the stability constant (K) and the molar absorptivity (ε) of each complex are then put into the DATA file.

The program works by reading the initial K and ε values into the main program and passing them to ADMIRL where they are used to calculate a set of "data."* This calculated data has the same pH values as the experimental data, but the absorption values are different. The calculated absorption values (CABS) are then compared to the experimental absorption values in subroutine FUNCT. The sum of the squares

*In essence, the computer produces what the absorption values for the samples would be if the assumed complex species existed and if they had the inputted stability constants and molar absorptivities.

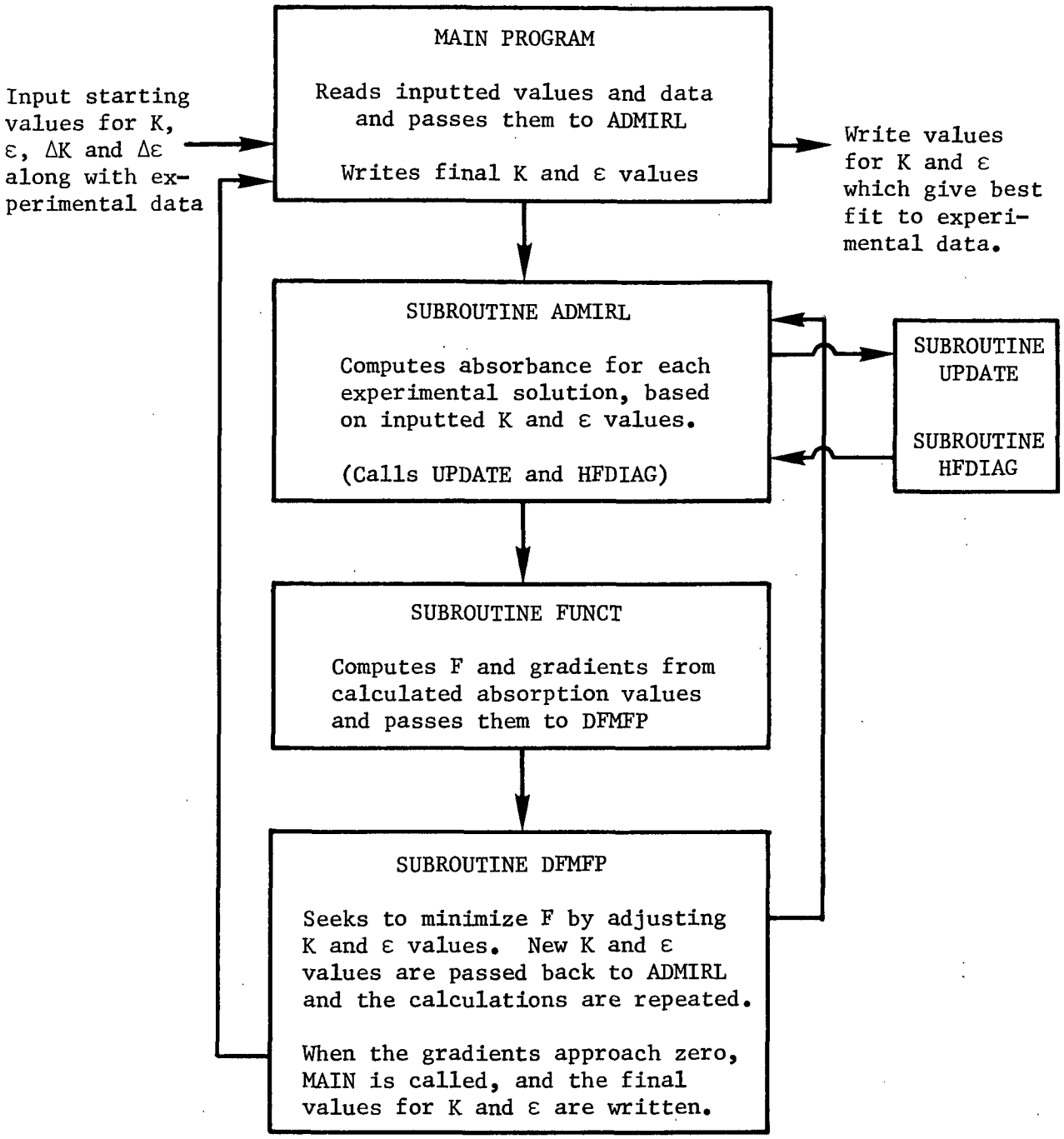


Figure 19. Diagram for Computer Program to Determine Stability Constants. Subroutine ADMIRL Solves up to 20 Nonlinear Equations Simultaneously

of the differences (F in the program, S in the text) is then minimized by subroutine DFMFP by slightly adjusting the K and ε values. DFMFP uses the Fletcher Powell routine (which is a modified version of the steepest descent method) to achieve the function minimum. The K and ε values which cause the function to reach a minimum are taken to be the best values.

```
/FILE DISK=(1,TEMP20),VOL=SYSFL1,DISP=(OLD,KEEP)
/JOB GO,TIME=99
      DIMENSION ABSB(35),X(2),G(2),H(22)
      DOUBLE PRECISION ABSB,DELOK1,DELOE3,X,F,G,H
      READ(5,101)DELOK1,DELOE3
      READ (5,102) (ABSB(II), II = 1,35)
      READ (5,103) (X(I), I = 1,2)
      READ(5,104) N,LIMIT
      READ(5,105) EST,EPS
      CALL DFMFP(DELOK1,DELOE3,ABSB,X,N,LIMIT,EST,EPS,F,G,IER,H)
  101 FORMAT (2F8.5)
  102 FORMAT (10F8.5)
  103 FORMAT (2F8.5)
  104 FORMAT (2I5)
  105 FORMAT (2E15.7)
      CALL EXIT
      END
```

```
      SUBROUTINE FUNCT(DELOK1,DELOE3,ABSB,X,F,G)
      DIMENSION ABSB(35),X(2),G(2),CABS(35),DELABS(35),BIGS(5)
      DOUBLE PRECISION ABSB,DELOK1,DELOE3,X,F,G,AK1,EP3,ALOGK1,ALOGE3,
     *ACIF,CABS,DELABS,BIGS
      ALOGK1 = X(1)
      ALOGE3 = X(2)
      J = 1
    6 AK1 = 10.**ALOGK1
      EP3 = 10.**ALOGE3
      CALL ADMIRL(AK1,EP3,CABS)
      DO 5 JJ = 1,35
    5 DELABS(JJ) = (ABSB(JJ)-CABS(JJ))**2
      WRITE (6,7000) CABS
C     WRITE (6,7000) DELABS
C7000 FORMAT (F12.5)
      BIGS(J) = 0.
      DO 9 JJ = 1,35
    9 BIGS(J) = DELABS(JJ) + BIGS(J)
      J = J + 1
      GO TO (10,10,11,14,15,18),J
   18 GO TO 7
   10 ALOGK1 = X(1) + DELOK1
      GO TO 6
   11 ALOGK1 = X(1) - DELOK1
      GO TO 6
   14 ALOGK1 = X(1)
      ALOGE3 = X(2) + DELOE3
      GO TO 6
   15 ALOGE3 = X(2) - DELOE3
      GO TO 6
    7 F = BIGS(1)
      G(1) = (BIGS(2)-BIGS(3))/(2.*DELOK1)
      G(2) = (BIGS(4)-BIGS(5))/(2.*DELOE3)
      WRITE (6,903) F,G(1),G(2)
      WRITE (6,904) X(1),X(2)
  903 FORMAT ('F = ',E15.7,'  G(1) = ',E15.7,'  G(2) = ',E15.7)
  904 FORMAT ('X(1) =',F12.5,'  X(2) =',F12.5)
      RETURN
      END
```

```
      SUBROUTINE DFMFP (DELOK1,DELOE3,ABSB,X,N,LIMIT,EST,EPS,F,G,IER,H)
C                                                                       DFMF 780
C        DIMENSIONED DUMMY VARIABLES                                    DFMF 790
      DIMENSION ABSB(35),X(2),G(2),H(22)
      DOUBLE PRECISION DELOK1,DELOE3,ABSB,X,F,G,H,ALPHA,Z,DX,DY
C                                                                       DFMF 830
C        COMPUTE FUNCTION VALUE AND GRADIENT VECTOR FOR INITIAL ARGUMENTDFMF 840
      CALL FUNCT(DELOK1,DELOE3,ABSB,X,F,G)
                                                                        DFMF 860
C        RESET ITERATION COUNTER AND GENERATE IDENTITY MATRIX           DFMF 870
      IER=0                                                             DFMF 880
      KOUNT=0                                                           DFMF 890
      N2=N+N                                                            DFMF 900
      N3=N2+N                                                           DFMF 910
      N31=N3+1                                                          DFMF 920
    1 K=N31                                                             DFMF 930
      DO 4 J=1,N                                                        DFMF 940
      H(K)=1.D0                                                         DFMF 950
      NJ=N-J                                                            DFMF 960
      IF(NJ)5,5,2                                                       DFMF 970
    2 DO 3 L=1,NJ                                                       DFMF 980
      KL=K+L                                                            DFMF 990
    3 H(KL)=0.D0                                                        DFMF1000
    4 K=KL+1                                                            DFMF1010
                                                                        DFMF1020
C        START ITERATION LOOP                                           DFMF1030
    5 KOUNT=KOUNT +1                                                    DFMF1040
C                                                                       DFMF1050
C        SAVE FUNCTION VALUE, ARGUMENT VECTOR AND GRADIENT VECTOR       DFMF1060
      OLDF=F                                                            DFMF1070
      DO 9 J=1,N                                                        DFMF1080
      K=N+J                                                             DFMF1090
      H(K)=G(J)                                                         DFMF1100
      K=K+N                                                             DFMF1110
      H(K)=X(J)                                                         DFMF1120
                                                                        DFMF1130
C        DETERMINE DIRECTION VECTOR H                                   DFMF1140
      K=J+N3                                                            DFMF1150
      T=0.DO                                                            DFMF1160
      DO 8 L=1,N                                                        DFMF1170
      T=T-G(L)*H(K)                                                     DFMF1180
      IF(L-J)6,7,7                                                      DFMF1190
    6 K=K+N-L                                                           DFMF1200
      GO TO 8                                                           DFMF1210
    7 K=K+1                                                             DFMF1220
    8 CONTINUE                                                          DFMF1230
    9 H(J)=T                                                            DFMF1240
                                                                        DFMF1250
C        CHECK WHETHER FUNCTION WILL DECREASE STEPPING ALONG H.         DFMF1260
      DY=0.D0                                                           DFMF1270
      HNRM=0.DO                                                         DFMF1280
      GNRM=0.D0                                                         DFMF1290
                                                                        DFMF1300
C        CALCULATE DIRECTIONAL DERIVATIVE AND TESTVALUES FOR DIRECTION  DFMF1310
C        VECTOR H AND GRADIENT VECTOR G.                                DFMF1320
      DO 10 J=1,N                                                       DFMF1330
      HNRM=HNRM+DABS(H(J))                                              DFMF1340
      GNRM=GNRM+DABS(G(J))                                              DFMF1350
   10 DY=DY+H(J)*G(J)                                                   DFMF1360
                                                                        DFMF1370
C        REPEAT SEARCH IN DIRECTION OF STEEPEST DESCENT IF DIRECTIONAL  DFMF1380
C        DERIVATIVE APPEARS TO BE POSITIVE OR ZERO.                     DFMF1390
      IF(DY)11,51,51                                                    DFMF1400
C                                                                       DFMF1410
C        REPEAT SEARCH IN DIRECTION OF STEEPEST DESCENT IF DIRECTION    DFMF1420
C        VECTOR H IS SMALL COMPARED TO GRADIENT VECTOR G.               DFMF1430
   11 IF(HNRM/GNRM-EPS)51,51,12                                         DFMF1440
```

```
C                                                                       DFMF1450
C        SEARCH MINIMUM ALONG DIRECTION H                               DFMF1460
C                                                                       DFMF1470
C        SEARCH ALONG H FOR POSITIVE DIRECTIONAL DERIVATIVE             DFMF1480
   12 FY=F                                                              DFMF1490
      ALFA=2.D0*(EST-F)/DY                                              DFMF1500
      AMBDA=1.D0                                                        DFMF1510
C                                                                       DFMF1520
C        USE ESTIMATE FOR STEPSIZE ONLY IF IT IS POSITIVE AND LESS THAN DFMF1530
C        1. OTHERWISE TAKE 1. AS STEPSIZE                               DFMF1540
      IF(ALFA)15,15,13                                                  DFMF1550
   13 IF(ALFA-AMBDA)14,15,15                                            DFMF1560
   14 AMBDA=ALFA                                                        DFMF1570
   15 ALFA=0.D0                                                         DFMF1580
C                                                                       DFMF1590
C        SAVE FUNCTION AND DERIVATIVE VALUES FOR OLD ARGUMENT           DFMF1600
   16 FX=FY                                                             DFMF1610
      DX=DY                                                             DFMF1620
C                                                                       DFMF1630
C        STEP ARGUMENT ALONG H                                          DFMF1640
      DO 17 I=1,N                                                       DFMF1650
   17 X(I)=X(I)+AMBDA*H(I)                                              DFMF1660
C                                                                       DFMF1670
C        COMPUTE FUNCTION VALUE AND GRADIENT FOR NEW ARGUMENT           DFMF1680
      CALL FUNCT(DELOK1,DELOE3,ABSB,X,F,G)                              
      FY=F                                                              DFMF1700
C                                                                       DFMF1710
C        COMPUTE DIRECTIONAL DERIVATIVE DY FOR NEW ARGUMENT.  TERMINATE DFMF1720
C        SEARCH, IF DY IS POSITIVE. IF DY IS ZERO THE MINIMUM IS FOUND  DFMF1730
      DY=0.D0                                                           DFMF1740
      DO 18 I=1,N                                                       DFMF1750
   18 DY=DY+G(I)*H(I)                                                   DFMF1760
      IF(DY)19,36,22                                                    DFMF1770
C                                                                       DFMF1780
C        TERMINATE SEARCH ALSO IF THE FUNCTION VALUE INDICATES THAT     DFMF1790
C        A MINIMUM HAS BEEN PASSED                                      DFMF1800
   19 IF(FY-FX)20,22,22                                                 DFMF1810
C                                                                       DFMF1820
C        REPEAT SEARCH AND DOUBLE STEPSIZE FOR FURTHER SEARCHES         DFMF1830
   20 AMBDA=AMBDA+ALFA                                                  DFMF1840
      ALFA=AMBDA                                                        DFMF1850
C        END OF SEARCH LOOP                                             DFMF1860
C                                                                       DFMF1870
C        TERMINATE IF THE CHANGE IN ARGUMENT GETS VERY LARGE            DFMF1880
      IF(HNRM*AMBDA-1.D10)16,16,21                                      DFMF1890
C                                                                       DFMF1900
C        LINEAR SEARCH TECHNIQUE INDICATES THAT NO MINIMUM EXISTS       DFMF1910
   21 IER=2                                                             DFMF1920
      RETURN                                                            DFMF1930
C                                                                       DFMF1940
C        INTERPOLATE CUBICALLY IN THE INTERVAL DEFINED BY THE SEARCH    DFMF1950
C        ABOVE AND COMPUTE THE ARGUMENT X FOR WHICH THE INTERPOLATION   DFMF1960
C        POLYNOMIAL IS MINIMIZED                                        DFMF1970
   22 T=0.D0                                                            DFMF1980
   23 IF(AMBDA)24,36,24                                                 DFMF1990
   24 Z=3.D0*(FX-FY)/AMBDA+DX+DY                                        DFMF2000
      ALFA=DMAX1(DABS(Z),DABS(DX),DABS(DY))                             DFMF2010
      DALFA=Z/ALFA                                                      DFMF2020
      DALFA=DALFA*DALFA-DX/ALFA*DY/ALFA                                 DFMF2030
      IF(DALFA)51,25,25                                                 DFMF2040
   25 W=ALFA*DSQRT(DALFA)                                               DFMF2050
      ALFA=DY-DX+W+W                                                    DFMF2060
      IF(ALFA) 250,251,250                                              DFMF2061
  250 ALFA=(DY-Z+W)/ALFA                                                DFMF2062
      GO TO 252                                                         DFMF2063
  251 ALFA=(Z+DY-W)/(Z+DX+Z+DY)                                         DFMF2064
  252 ALFA=ALFA*AMBDA                                                   DFMF2065
      DO 26 I=1,N                                                       DFMF2070
   26 X(I)=X(I)+(T-ALFA)*H(I)                                           DFMF2090
```

```
C                                                                       DFMF2090
C       TERMINATE, IF THE VALUE OF THE ACTUAL FUNCTION AT X IS LESS     DFMF2100
C       THAN THE FUNCTION VALUES AT THE INTERVAL ENDS. OTHERWISE REDUCE DFMF2110
C       THE INTERVAL BY CHOOSING ONE END-POINT EQUAL TO X AND REPEAT    DFMF2120
C       THE INTERPOLATION. WHICH END-POINT IS CHOOSEN DEPENDS ON THE    DFMF2130
C       VALUE OF THE FUNCTION AND ITS GRADIENT AT X                     DFMF2140
C                                                                       DFMF2150
      CALL FUNCT(DELOK1,DELOE3,ABSB,X,F,G)
      IF(F-FX)27,27,28                                                  DFMF2170
   27 IF(F-FY)36,36,28                                                  DFMF2180
   28 DALFA=0.D0                                                        DFMF2190
      DO 29 I=1,N                                                       DFMF2200
   29 DALFA=DALFA+G(I)*H(I)                                             DFMF2210
      IF(DALFA)30,33,33                                                 DFMF2220
   30 IF(F-FX)32,31,33                                                  DFMF2230
   31 IF(DX-DALFA)32,36,32                                              DFMF2240
   32 FX=F                                                              DFMF2250
      DX=DALFA                                                          DFMF2260
      T=ALFA                                                            DFMF2270
      AMBDA=ALFA                                                        DFMF2280
      GO TO 23                                                          DFMF2290
   33 IF(FY-F)35,34,35                                                  DFMF2300
   34 IF(DY-DALFA)35,36,35                                              DFMF2310
   35 FY=F                                                              DFMF2320
      DY=DALFA                                                          DFMF2330
      AMBDA=AMBDA-ALFA                                                  DFMF2340
      GO TO 22                                                          DFMF2350
C                                                                       DFMF2360
C       TERMINATE, IF FUNCTION HAS NOT DECREASED DURING LAST ITERATION  DFMF2370
   36 IF(OLDF-F+EPS)51,38,38                                            DFMF2380
C                                                                       DFMF2390
C       COMPUTE DIFFERENCE VECTORS OF ARGUMENT AND GRADIENT FROM        DFMF2400
C       TWO CONSECUTIVE ITERATIONS                                      DFMF2410
   38 DO 37 J=1,N                                                       DFMF2420
      K=N+J                                                             DFMF2430
      H(K)=G(J)-H(K)                                                    DFMF2440
      K=N+K                                                             DFMF2450
   37 H(K)=X(J)-H(K)                                                    DFMF2460
C                                                                       DFMF2470
C       TEST LENGTH OF ARGUMENT DIFFERENCE VECTOR AND DIRECTION VECTOR  DFMF2480
C       IF AT LEAST N ITERATIONS HAVE BEEN EXECUTED. TERMINATE, IF      DFMF2490
C       BOTH ARE LESS THAN EPS                                          DFMF2500
      IER=0                                                             DFMF2510
      IF(KOUNT-N)42,39,39                                               DFMF2520
   39 T=0.D0                                                            DFMF2530
      Z=0.D0                                                            DFMF2540
      DO 40 J=1,N                                                       DFMF2550
      K=N+J                                                             DFMF2560
      W=H(K)                                                            DFMF2570
      K=K+N                                                             DFMF2580
      T=T+DABS(H(K))                                                    DFMF2590
   40 Z=Z+W*H(K)                                                        DFMF2600
      IF(HNRM-EPS)41,41,42                                              DFMF2610
   41 IF(T-EPS)56,56,42                                                 DFMF2620
C                                                                       DFMF2630
C       TERMINATE, IF NUMBER OF ITERATIONS WOULD EXCEED  LIMIT          DFMF2640
   42 IF(KOUNT-LIMIT)43,50,50                                           DFMF2650
C                                                                       DFMF2660
C       PREPARE UPDATING OF MATRIX H                                    DFMF2670
   43 ALFA=0.D0                                                         DFMF2680
      DO 47 J=1,N                                                       DFMF2690
      K=J+N3                                                            DFMF2700
```

```
      W=0.DO                                                          DFMF2720
      DO 46 L=1,N                                                     DFMF2730
      KL=N+L                                                          DFMF2740
      W=W+H(KL)*H(K)                                                  DFMF2750
      IF(L-J)44,45,45                                                 DFMF2760
   44 K=K+N-L                                                         DFMF2770
      GO TO 46                                                        DFMF2780
   45 K=K+1                                                           DFMF2790
   46 CONTINUE                                                        DFMF2800
      K=N+J                                                           DFMF2810
      ALFA=ALFA+W*H(K)                                                DFMF2820
   47 H(J)=W                                                          DFMF2830
C                                                                     DFMF2840
C        REPEAT SEARCH IN DIRECTION OF STEEPEST DESCENT IF RESULTS    DFMF2850
C        ARE NOT SATISFACTORY                                         DFMF2860
      IF(Z*ALFA)48,1,48                                               DFMF2870
C                                                                     DFMF2880
C        UPDATE MATRIX H                                              DFMF2890
   48 K=N31                                                           DFMF2900
      DO 49 L=1,N                                                     DFMF2910
      KL=N2+L                                                         DFMF2920
      DO 49 J=L,N                                                     DFMF2930
      NJ=N2+J                                                         DFMF2940
      H(K)=H(K)+H(KL)*H(NJ)/Z-H(L)*H(J)/ALFA                          DFMF2950
   49 K=K+1                                                           DFMF2960
      GO TO 5                                                         DFMF2970
C        END OF ITERATION LOOP                                        DFMF2980
C                                                                     DFMF3000
   50 IER=1                                                           DFMF3010
      RETURN                                                          DFMF2990
C        NO CONVERGENCE AFTER  LIMIT  ITERATIONS                      DFMF3020
C        RESTORE OLD VALUES OF FUNCTION AND ARGUMENTS                 DFMF3030
   51 DO 52 J=1,N                                                     DFMF3040
      K=N2+J                                                          DFMF3050
   52 X(J)=H(K)                                                       DFMF3060
      CALL FUNCT(DELOK1,DELCE3,ABSB,X,F,G)                            DFMF3080
C                                                                     DFMF3090
C        REPEAT SEARCH IN DIRECTION OF STEEPEST DESCENT IF DERIVATIVE DFMF3100
C        FAILS TO BE SUFFICIENTLY SMALL                               DFMF3110
      IF(GNRM-EPS)55,55,53                                            DFMF3120
C                                                                     DFMF3130
C        TEST FOR REPEATED FAILURE OF ITERATION                       DFMF3140
   53 IF(IER)56,54,54                                                 DFMF3150
   54 IER=-1                                                          DFMF3160
      GOTO 1                                                          DFMF3170
   55 IER=0                                                           DFMF3180
   56 RETURN                                                          DFMF3190
      END
```

```
      SUBROUTINE ADMIRL(AK1,EP3,CABS)
      DIMENSION A(20,21),X(20),Y(20)
      DIMENSION TM(35),TL(35),S(35),CABS(35)
      DOUBLE PRECISION A,X,TM,TL,S,CABS,Y
      COMMON A,X,TM,TL,S,N
      DIMENSION LABEL(8)
      COMMON INDEX, NGROUP, NSPACE, LABEL
      REWIND 1
      N = 5
    1 READ (1,302) QUANT, LABEL
      READ (1,9C01) NN
 9C01 FORMAT(I10)
      READ (1,9C00) (TM(II),II = 1,35)
      READ (1,9C00) (TL(II),II = 1,35)
      READ (1,9C00) ( S(II),II = 1,35)
C     WRITE (6,7002) TM,TL,S
C7C02 FORMAT(9F8.5)
 9C00 FORMAT(10F8.5)
      DO 7C5 I = 1,N
  705 READ (1,307) Y(I)
  307 FORMAT (E15.7)
    2 DO 15 JJ = NN,35
      DO 14 I = 1,N
   14 X(I) = Y(I)
      INDEX = 2
      CALL UPDATE (JJ,AK1,EP3)
      CALL EFDIAG
      INDEX = 3
      L = N + 1
   20 CALL UPDATE (JJ,AK1,EP3)
      CALL EFDIAG
      SAVE = 0.0
      DO 5 I = 1,N
      TEMP = A(I,L)
      SAVE = SAVE + TEMP * TEMP
    5 X(I) = X(I) + TEMP
      IF (SAVE-QUANT)6,6,20
    6 CALL UPDATE (JJ,AK1,EP3)
      NGROUP = N + 4
      NSPACE = 1
      CABS(JJ) = X(5)
      DO 8 I = 1,N
    8 TEMP = -A(I,L)
   15 CONTINUE
      RETURN
  302 FORMAT (E15.7,8A4)
      END
```

```
      SUBROUTINE UPDATE (JJ,AK1,EP3)
      DIMENSION A(20,21), X(20)
      DIMENSION TM(35),TL(35),S(35),DUM4(35)
      DOUBLE PRECISION A,X,TM,TL,S,AK1,EP3
      COMMON A,X,TM,TL,S,N
      DIMENSION LABEL(8)
      COMMON INDEX, NGROUP, NSPACE, LABEL
      GO TO (704, 704, 701), INDEX
C                GROUP A
C          THESE STATEMENTS SET THE VALUE OF  N  , PROVIDE FOR
           INPUT OF PARAMETERS, AND READ IN THE TRIAL SOLUTION
  704 NGROUP = N + 8
      NSPACE = 1
C     WRITE (6,8000)JJ
 8000 FORMAT(I3)
      WRITE (6,8001)TM,TL,S,AK1,EP3
 8001 FORMAT (5F15.8)
C                END OF GROUP A
      RETURN
                 GROUP B
           THESE STATEMENTS CALCULATE THE (NEGATIVES OF) THE
C          DISCREPANCIES
  701 DO 401 I =1,20
      DO 401 J =1,21
  401 A(I,J) = 0
      A(01,06) = TM(JJ)-X(1)-X(2)
      A(02,06) = TL(JJ)-X(2)-X(3)-X(4)
      A(03,06) = X(5)-X(3)*4898.-X(4)*3497.-X(2)*EP3
      A(04,06) = X(3)-S(JJ)*X(4)
      A(05,06) = AK1*X(1)*X(4)-X(2)
C     WRITE (6,8003)X(1),X(2),X(3),X(4),X(5)
C8003 FORMAT (5E15.7)
      A(01,01) = 1.
      A(01,02) = 1.
      A(02,02) = 1.
      A(02,03) = 1.
      A(02,04) = 1.
      A(03,02) = EP3
      A(03,03) = 4898.
      A(03,04) = 3497.
      A(03,05) = -1.
      A(04,03) = -1.
      A(04,04) = S(JJ)
      A(05,01) = -1.*AK1*X(4)
      A(05,02) = 1.
      A(05,04) = -1.*AK1*X(1)
                 END OF GROUP B
      RETURN
      END
```

```
      SUBROUTINE HFDIAG
      DIMENSION A(20,21), X(20)
      DIMENSION DUM1(35),DUM2(35),DUM3(35),DUM4(35)
      DOUBLE PRECISION A,X,DUM1,DUM2,DUM3,DUM4,P,Q
      COMMON A,X,DUM1,DUM2,DUM3,N
      DIMENSION LABEL(8)
      COMMON INDEX, NGROUP, NSPACE, LABEL
      GO TO (575, 575, 535), INDEX
  575 IF (N - 2)  515, 517, 516
  516 IF (N - 20)  517, 517, 515
  515 WRITE (6,307)
      WRITE (6,308)
      CALL EXIT
  517 NP1 = N + 1
      NM1 = N - 1
      RETURN
  535 DO 504  K = 1, NM1
      P = 0.0
      DO 508  I = K, N
      Q = A(I,K)
      IF (Q)  505, 506, 506
  505 Q = - Q
  506 IF (P - Q)  507, 508, 508
  507 P = Q
      L = I
  508 CONTINUE
      IF (K - L)  510, 512, 512
  510 DO 511  J = K, NP1
      Q = A(K,J)
      A(K,J) = A(L,J)
  511 A(L,J) = Q
  512 L = K + 1
      DO 504  I = L, N
      IF (A(K,K)) 404, 910, 404
  404 A(I,K) = A(I,K) / A(K,K)
      DO 504  J = L, NP1
  504 A(I,J) = A(I,J) - A(I,K) * A(K,J)
      A(N,NP1) = A(N,NP1) / A(N,N)
      DO 550  I = 1, NM1
      L = N - I
      DO 520  J = 1, I
      K = NP1 - J
  520 A(L,NP1) = A(L,NP1) - A(L,K) * A(K,NP1)
  550 A(L,NP1) = A(L,NP1) / A(L,L)
      RETURN
  910 WRITE (6,9000)K
 9000 FORMAT(' A(K,K) = 0', I10)
      DO 918 II = 1,20
  918 WRITE (6,9006) (A(II,JJ), JJ = 1,11)
      DO 919 II = 1,20
  919 WRITE (6,9006) (A(II,JJ), JJ = 12,21)
 9006 FORMAT(' ',11E11.4)
      CALL EXIT
  307 FORMAT (1H , 4X, 'ERROR  N  OUT OF RANGE')
  308 FORMAT (1H , 4X, 'CORRECT AND RECOMPILE  UPDATE')
      END
```

END CARD READ, JOB TERMINATED

APPENDIX II

DETERMINATION OF THE ACID DISSOCIATION CONSTANTS OF KC4S

The following figures (20-33) are plots of the experimental data points from which the acid dissociation constants of KC4S were determined. Each point of each plot represents a sample solution of KC4S at 0.92N ionic strength. The absorbance (at either 240 or 255 nm) and the pH of each sample were measured at the temperature noted on each plot. No calcium was present in any sample used to determine the pKas.

The vertical axis in each plot is the absorbance measured at the analytical wavelength. The horizontal axis pertains to the molar concentration of the more ionized species of KC4S (partially dissociated KC4S for pKa1, and totally dissociated KC4S for pKa2).

For pKa2, the equation plotted is Eq. (19) on page 17. For pKa1, LH (the partially dissociated KC4S) would be substituted for L (the totally dissociated species) and ε_2 (the molar absorptivity for the totally dissociated KC4S) would become ε_1. ε_1 would become ε_0 so the equation would read:

$$A = (\varepsilon_1 - \varepsilon_0)\ [LH_2] + \varepsilon_0\ [T_L] \qquad (27)$$

The computer program (Fig. 21 and 22) precedes the data plots. The subroutines which it calls that are not listed (MINMAX and PLOTR) are both standard programs contained in the computer library. The experimental data from which the pKa2 values were calculated is listed in Table VII.

The computer program works by starting with an initial guess for the pKa value which is intentionally low. Based on this assumed pKa, the amount of each of the ionic species of KC4S in each of the solutions was calculated (there are only two

```
/JCB GO
      DIMENSION UVA(20),AL1 (20), PH (20), ANAME (20), ALMAX(20)
C     UVA = ULTRAVIOLET ABSORBTION
C     AL1 = MONO-ANION CONCENTRATION
C     ALT = TOTAL LIGAND CONCENTRATION
C     PKA = INVERSE LOG OF ACID DISSOCIATION CONSTANT
C     DPKA = INCREMENTATION OF PKA
C     PKAMAX = HIGHEST VALUE OF PKA TO BE COMPUTED
C     PH = NEGATIVE LOG OF THE HYDROGEN ION CONCENTRATION
      N = 0
      NCOUNT = 0
      RMAX = 0.
      READ (5,103) ANAME
  103 FORMAT (20A4)
      READ (5,100) ALT, PKA, PKAMAX, DPKA, NPTS
  100 FORMAT (4F10.0, I2)
C     WRITE (6,8000) ALT, PKA, PKAMAX, DPKA, NPTS
C8000 FORMAT (4F10.0, I2)
      DO 1 I = 1,NPTS
      READ (5,100) UVA(I), PH(I)
    1 CONTINUE
    8 DO 10 I = 1,NPTS
      AL1(I) =  ALT/(1. +  10.**(PKA-PH(I)))
C     WRITE (6,5000) AL1(I)
C5000 FORMAT (F10.6)
   10 CONTINUE
      CALL LRANAL (UVA,AL1,NPTS,A,B,RXY)
      IF (RXY-RMAX) 2,2,3
    3 RMAX = RXY
      AMAX = A
      BMAX = B
      DO 75 I = 1,NPTS
      ALMAX(I) = AL1(I)
   75 CONTINUE
      PKAOPT = PKA
    2 CONTINUE
      PKA = PKA + DPKA
      IF(PKA-PKAMAX) 4,4,5
    4 NCOUNT = NCOUNT + 1
      IF(NCOUNT-10) 8,7,7
    7 WRITE (6,101) NCOUNT, RXY, PKA
  101 FORMAT (1X,'FOR',I4,' ITERATIONS, R = ',F10.6,/,1X,'PKA = ',
     XF8.4,/)
      NCOUNT = 0
      GO TO 8
    5 WRITE (6,104) ANAME
  104 FORMAT (///,20A4,/)
      WRITE (6,102) PKAOPT,AMAX,BMAX,RMAX
  102 FORMAT (1H,'FOR BEST FIT, PKA = 'F8.4,/,5X,'INTERCEPT = ',F12.6,
     X/,5X,'SLOPE = ',F12.1,/,5X,'LINEAR CORRELATION COEFFICIENT = ',
     XF10.6,///)
      CALL MINMAX (UVA,UMIN,UMAX,NPTS)
      JMAX = UMAX + 1.0
      UMAX = JMAX
      JMIN = UMIN - 1.0
      UMIN = JMIN
      JLMAX = 10000. * ALT + 1
      AAMAX = JLMAX
      AAMAX = AAMAX/10000.
      M = 0
      CALL PLOT (ALMAX,UVA,NPTS,0.,AAMAX,UMIN,UMAX,1,M)
      CALL EXIT
      END
```

Figure 20. Computer Program to Determine pKas

```
      SUBROUTINE LRANAL (UVA,AL1,NPTS,A,B,RXY)
      DIMENSION AL1(20),UVA(20)
      COUNT = 0.
      SIGX = C.
      SIGX2 = 0.
      SIGY = C.
      SIGY2 = 0.
      SIGXY = 0.
      BETA = C.0
      DO 1 J = 1,NPTS
      X = AL1(J)
      Y = UVA(J)
C     WRITE (6,6000) X,Y
C6000 FORMAT (F10.6)
      COUNT = COUNT + 1.
      SIGX = SIGX + X
      SIGX2 = SIGX2+X**2
      SIGY = SIGY + Y
      SIGY2 = SIGY2+Y**2
      SIGXY = SIGXY+X*Y
    1 CONTINUE
      SSX = (COUNT*SIGX2-(SIGX**2))/COUNT
      SSY = (COUNT*SIGY2-(SIGY**2))/COUNT
      SSXY = (COUNT*SIGXY-SIGX*SIGY)/COUNT
      B=SSXY/SSX
      S2XY=(SSY-(SSXY**2/SSX))/(COUNT-2.)
      A=SIGY/COUNT-(B*SIGX)/COUNT
      S2B=SQRT(S2XY/SSX)
      ROOT=SQRT(SSX*SSY)
      RXY=ABS(SSXY/ROOT)
      RETURN
      END
```

Figure 21. Computer Program to Compute Linear Regression Analysis

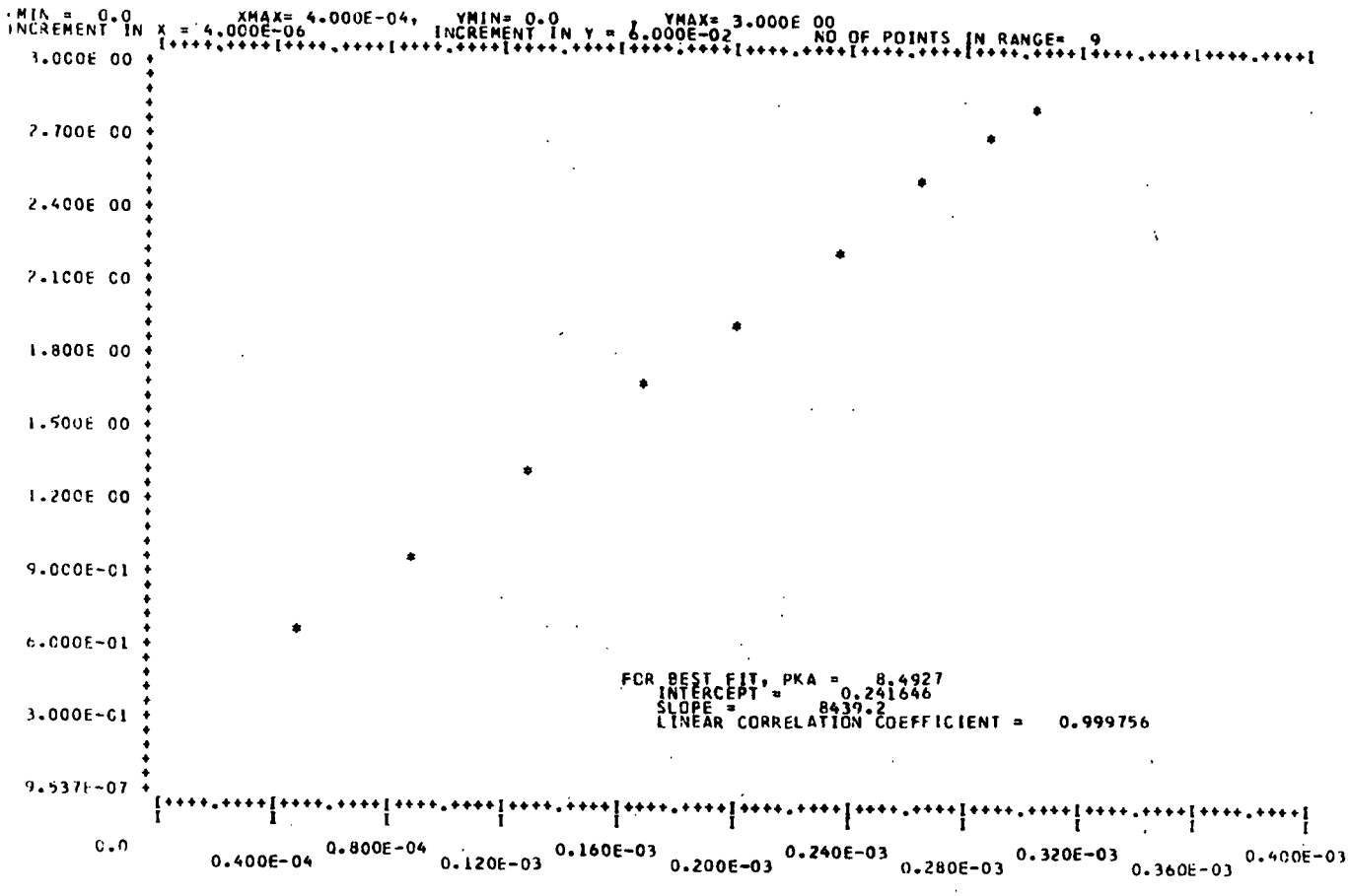


Figure 22. Plot of Data for Determination of pKa1 in 0.1N KCl at 255 nm and 20 Degrees

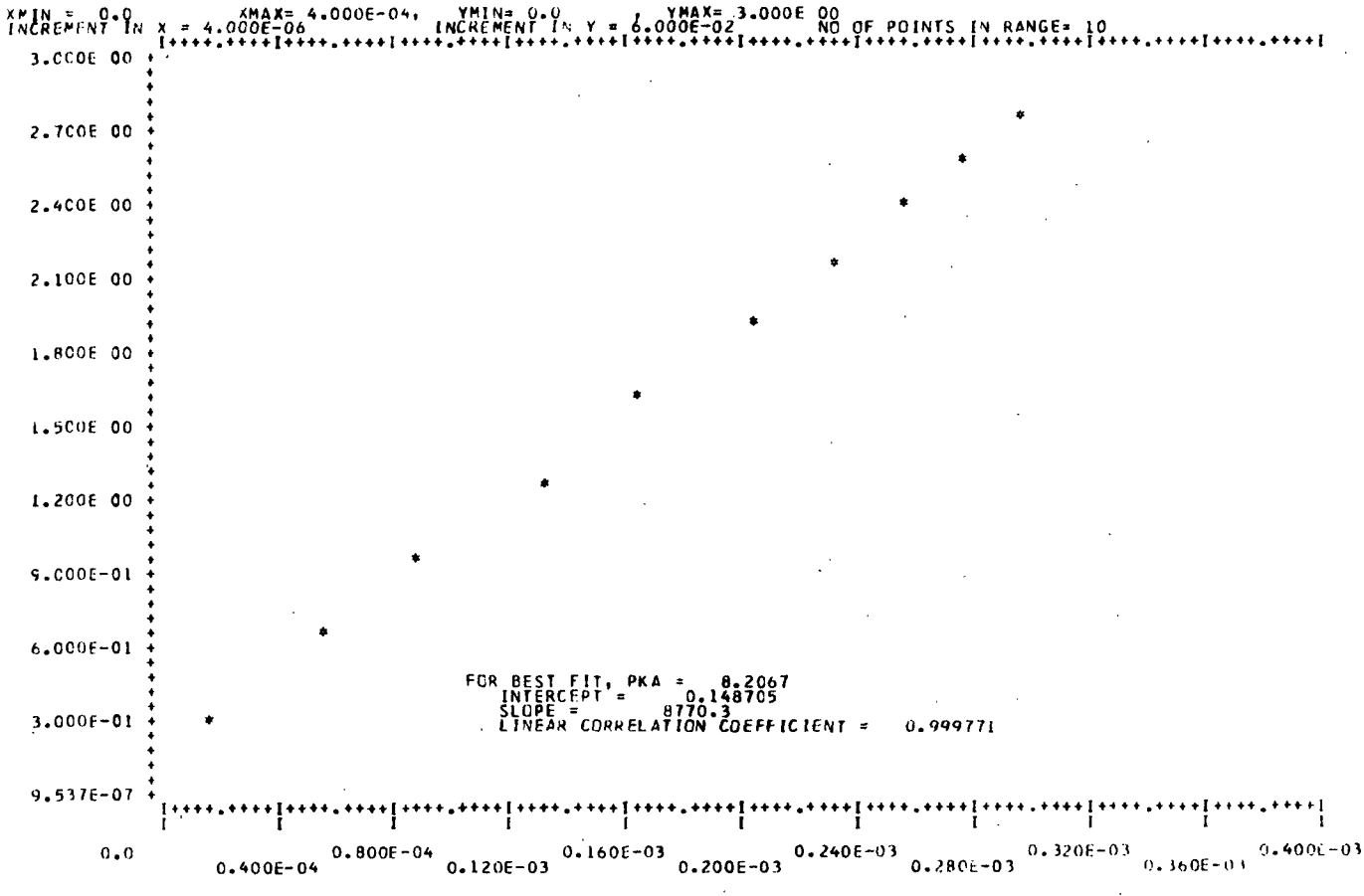


Figure 23. Plot of Data for Determination of pKa1 in 0.1N KCl at 255 nm and 40 Degrees

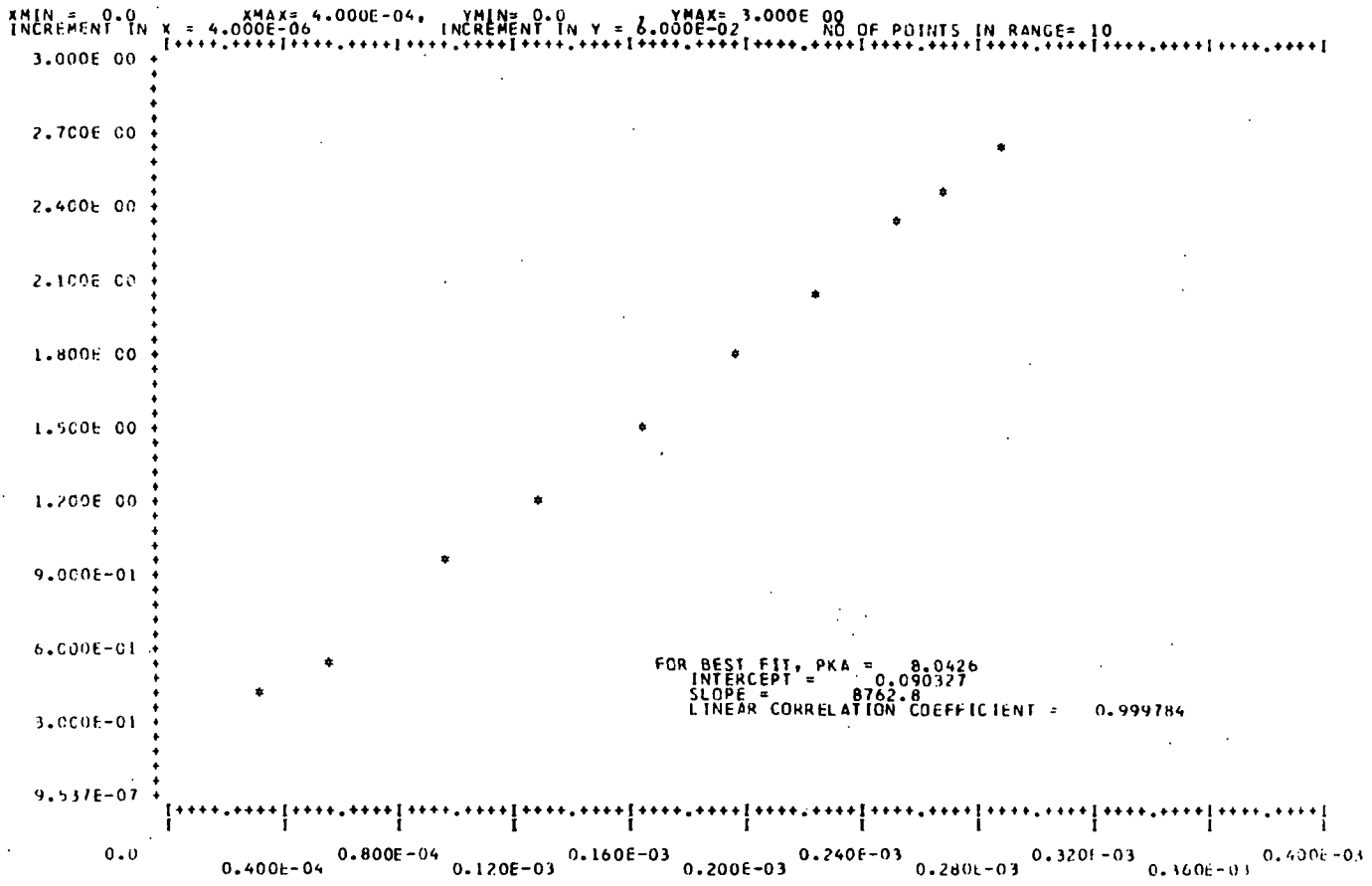


Figure 24. Plot of Data for Determination of pKa1 in 0.1N KCl at 255 nm and 60 Degrees

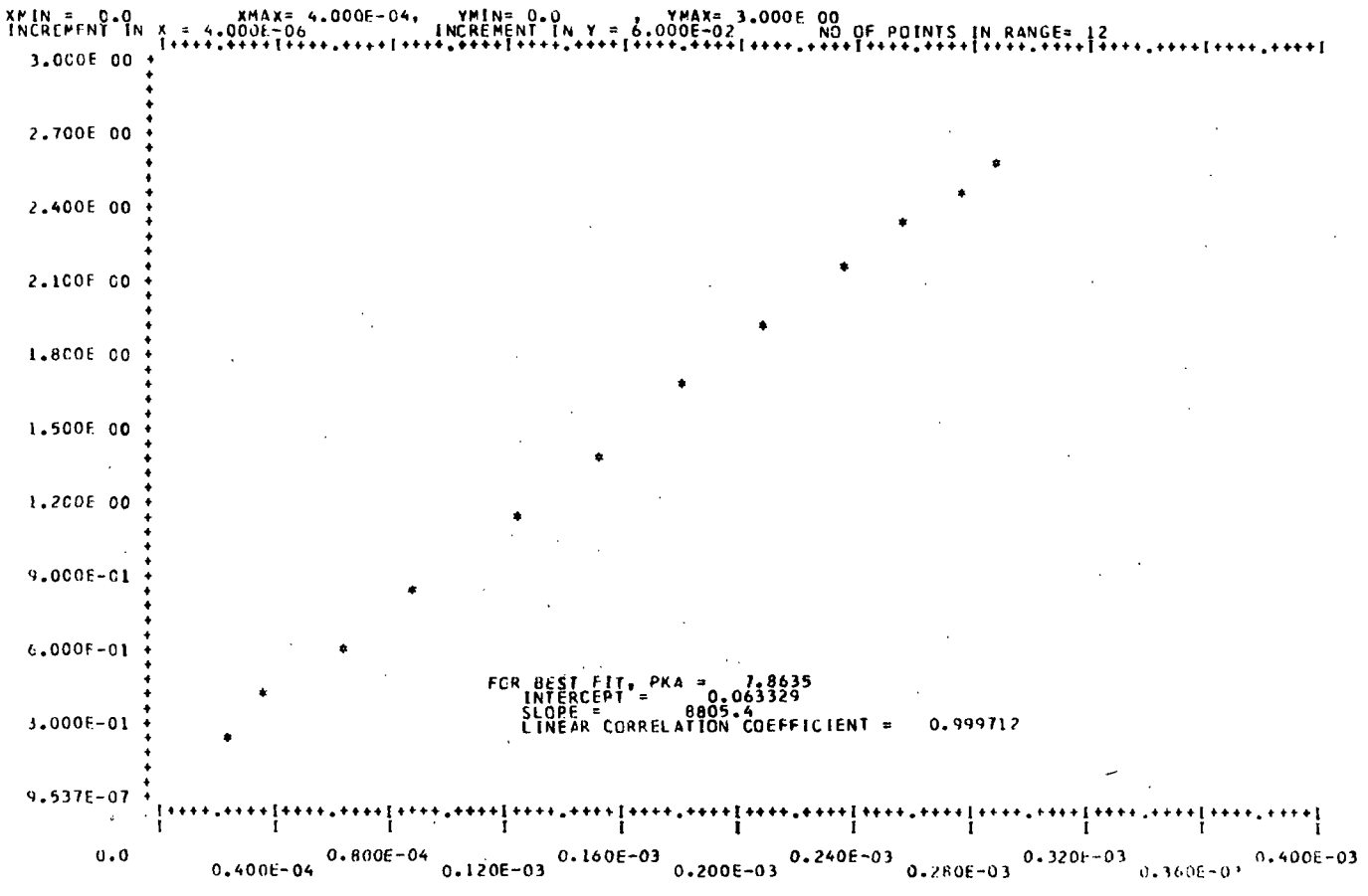


Figure 25. Plot of Data for Determination of pKa1 in 0.1N KCl at 255 nm and 80 Degrees

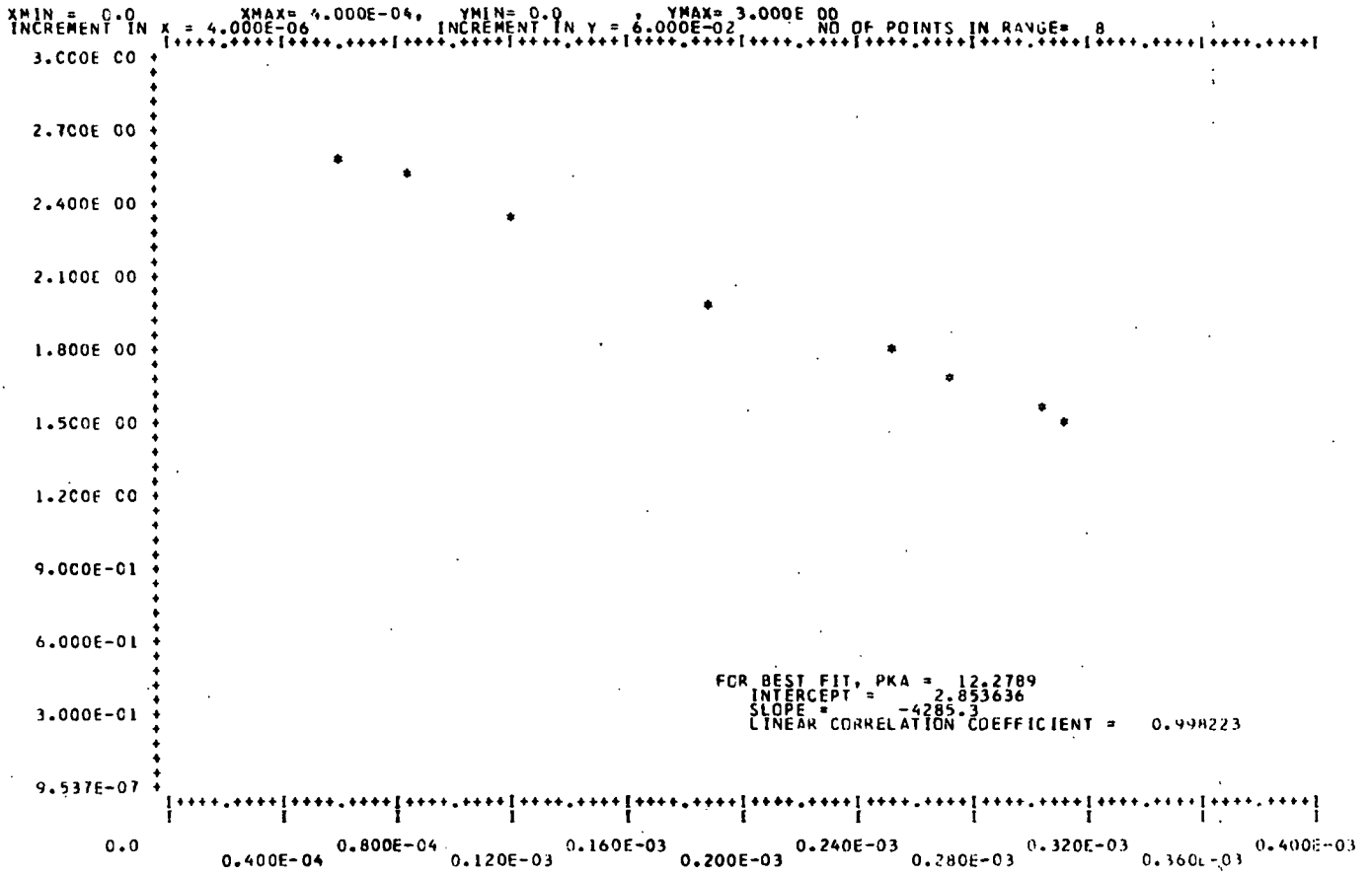


Figure 26. Plot of Data for Determination of pKa2 in 0.92N KCl at 255 nm and 20 Degrees

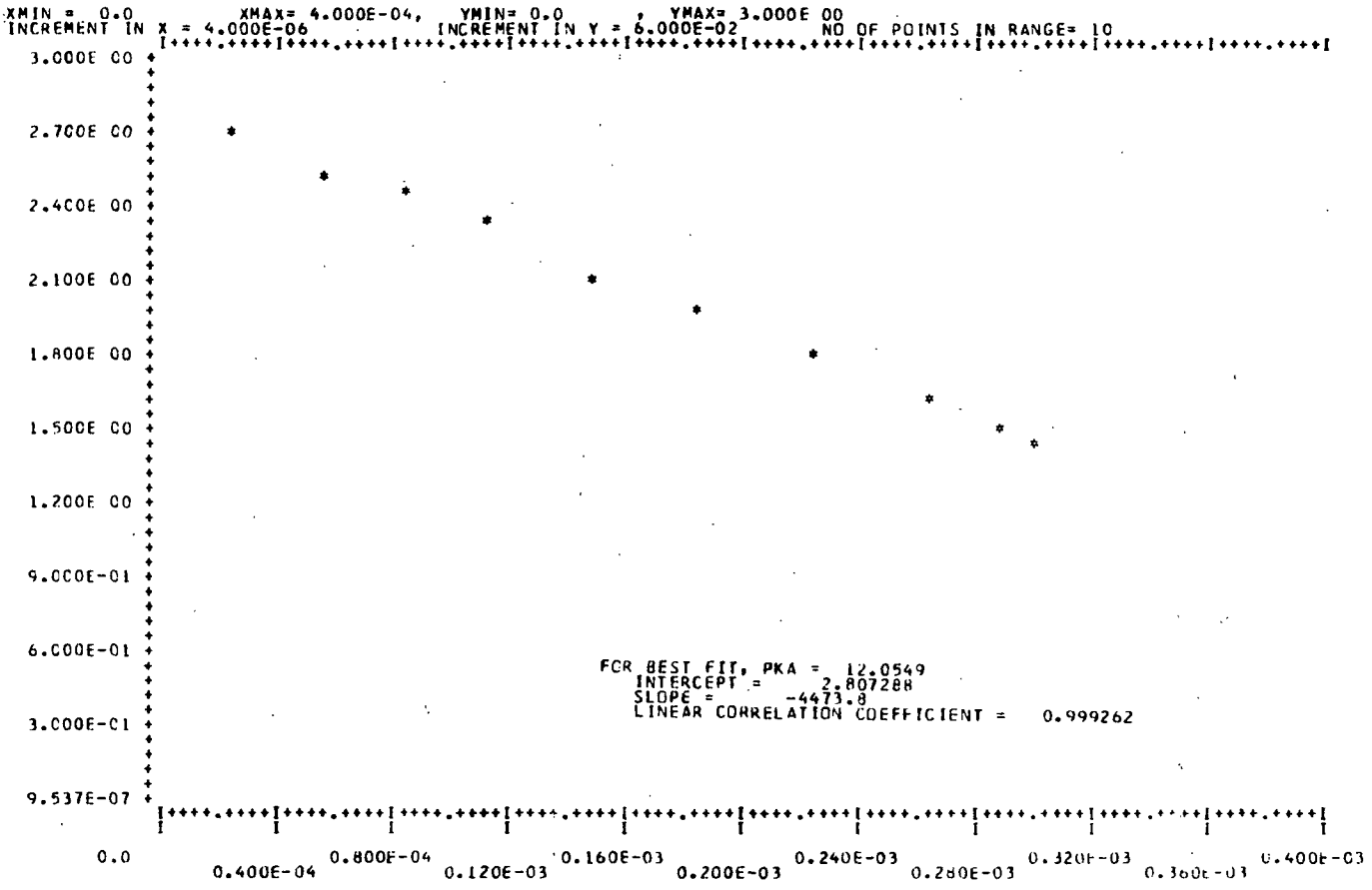


Figure 27. Plot of Data for Determination of pKa2 in 0.92N KCl at 255 nm and 40 Degrees

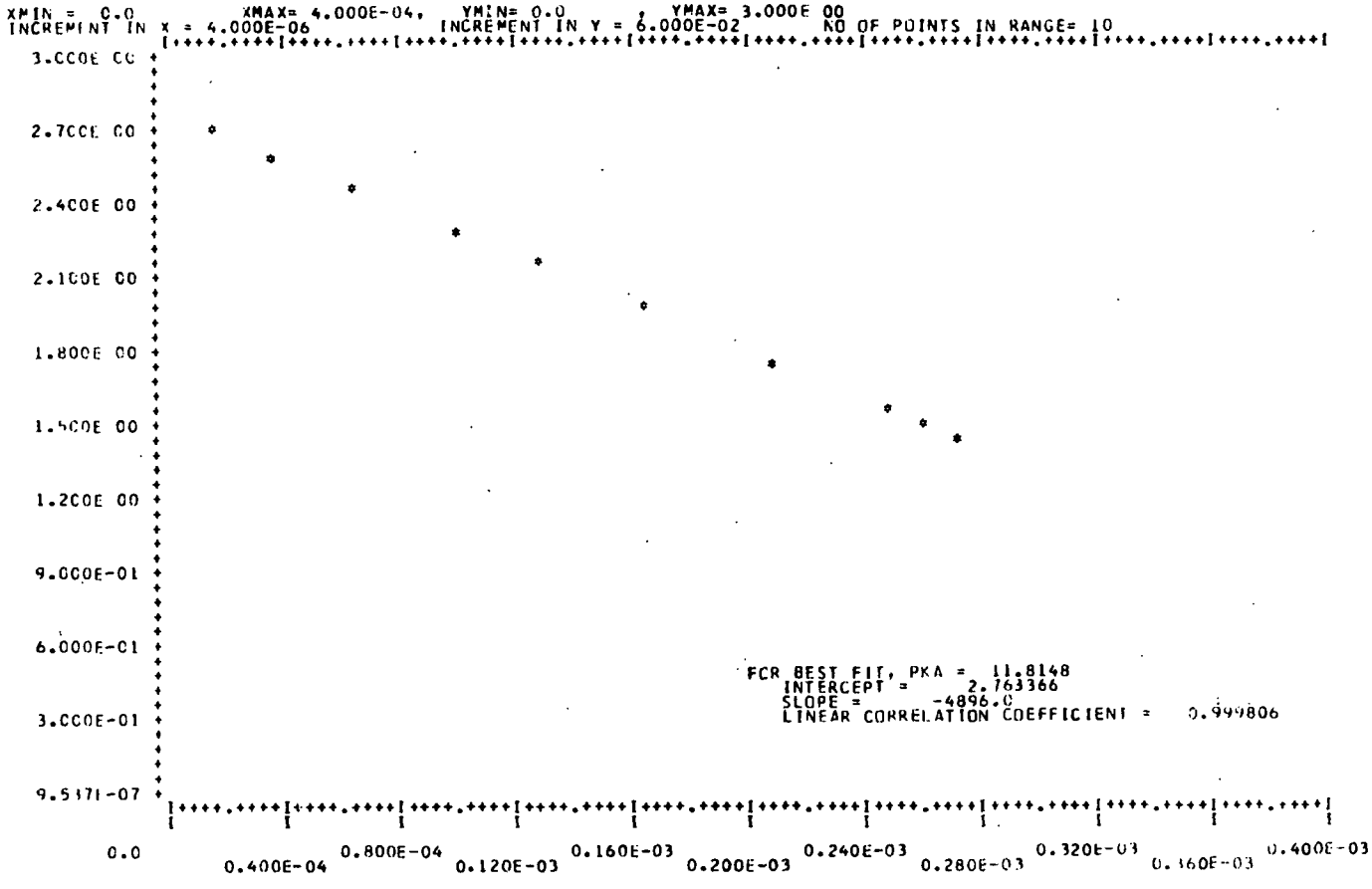


Figure 28. Plot of Data for Determination of pKa2 in 0.92N KCl at 255 nm and 60 Degrees

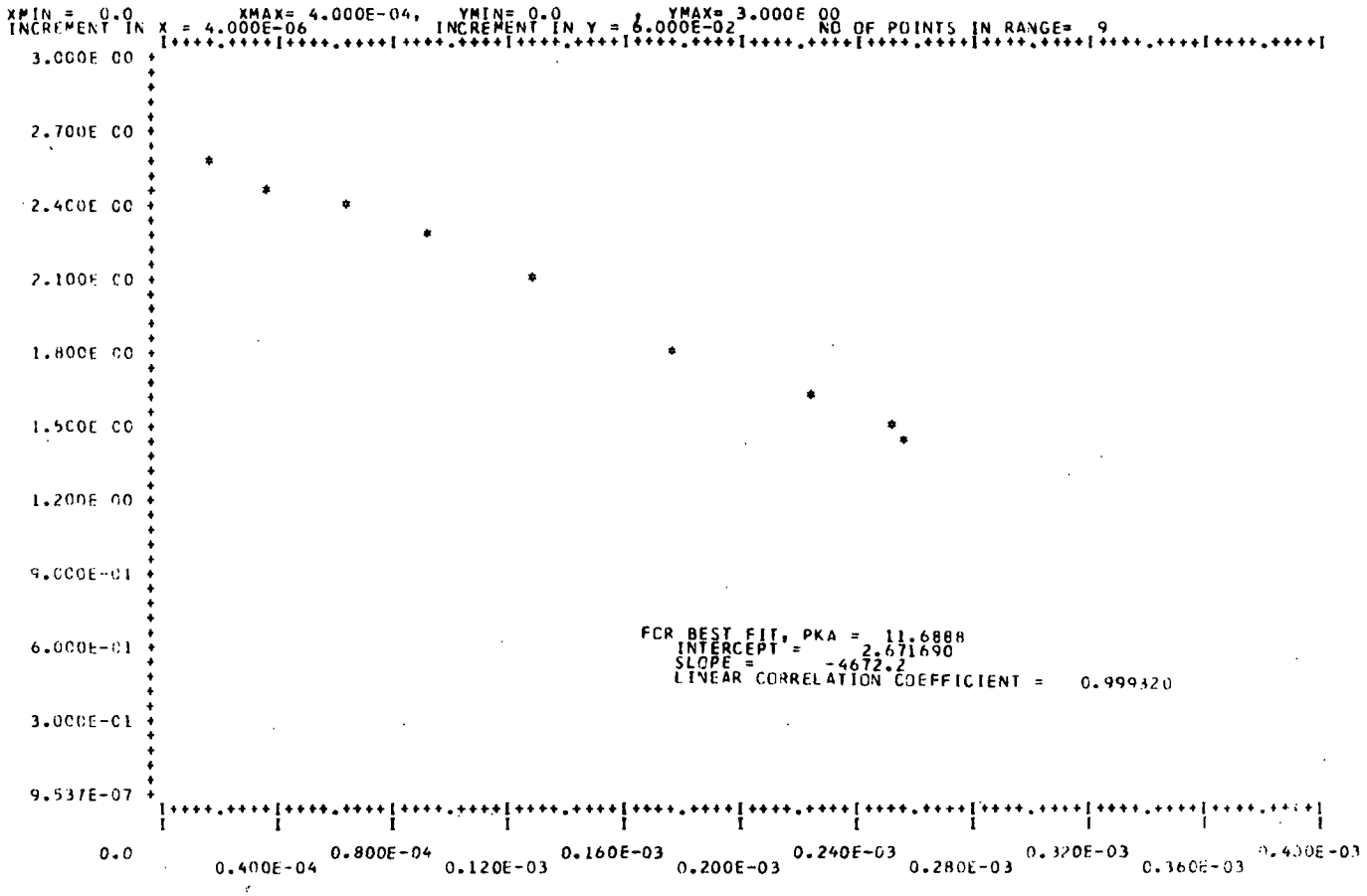


Figure 29. Plot of Data for Determination of pKa2 in 0.92N KCl at 255 nm and 80 Degrees

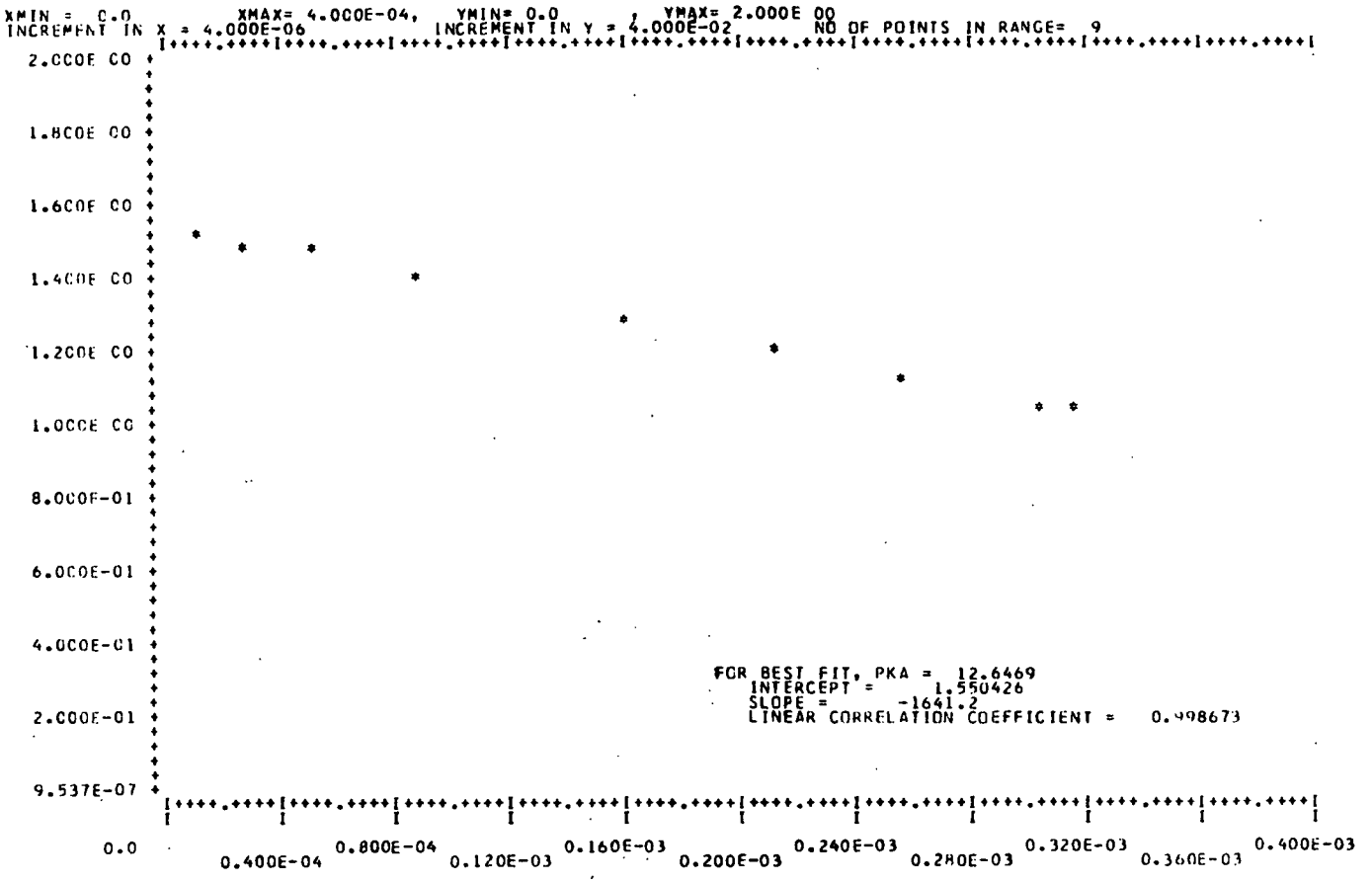


Figure 30. Plot of Data for Determination of pKa2 in 0.92N KCl at 240 nm and 5 Degrees

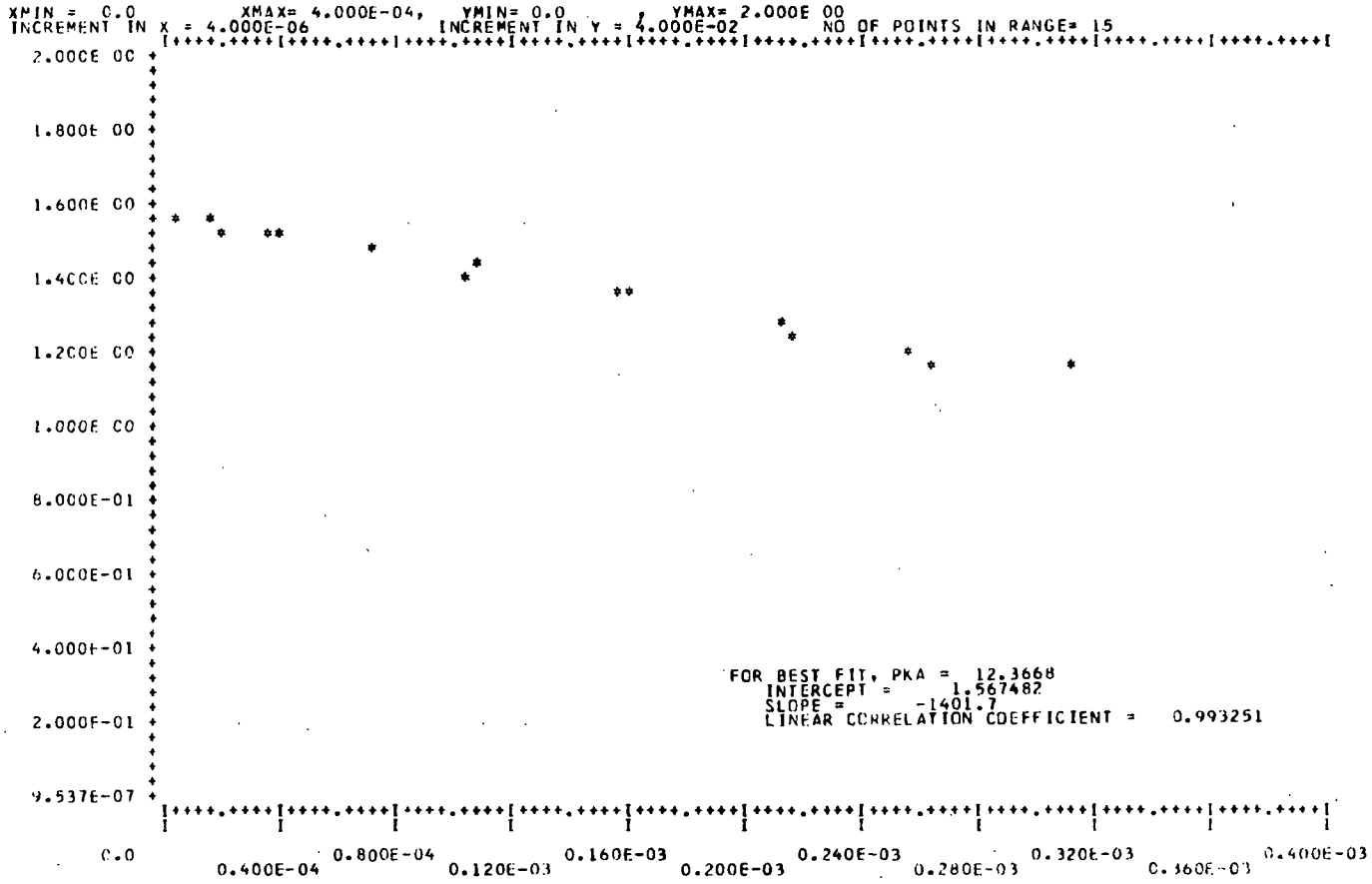


Figure 31. Plot of Data for Determination of pKa2 in 0.92N KCl at 240 nm and 20 Degrees

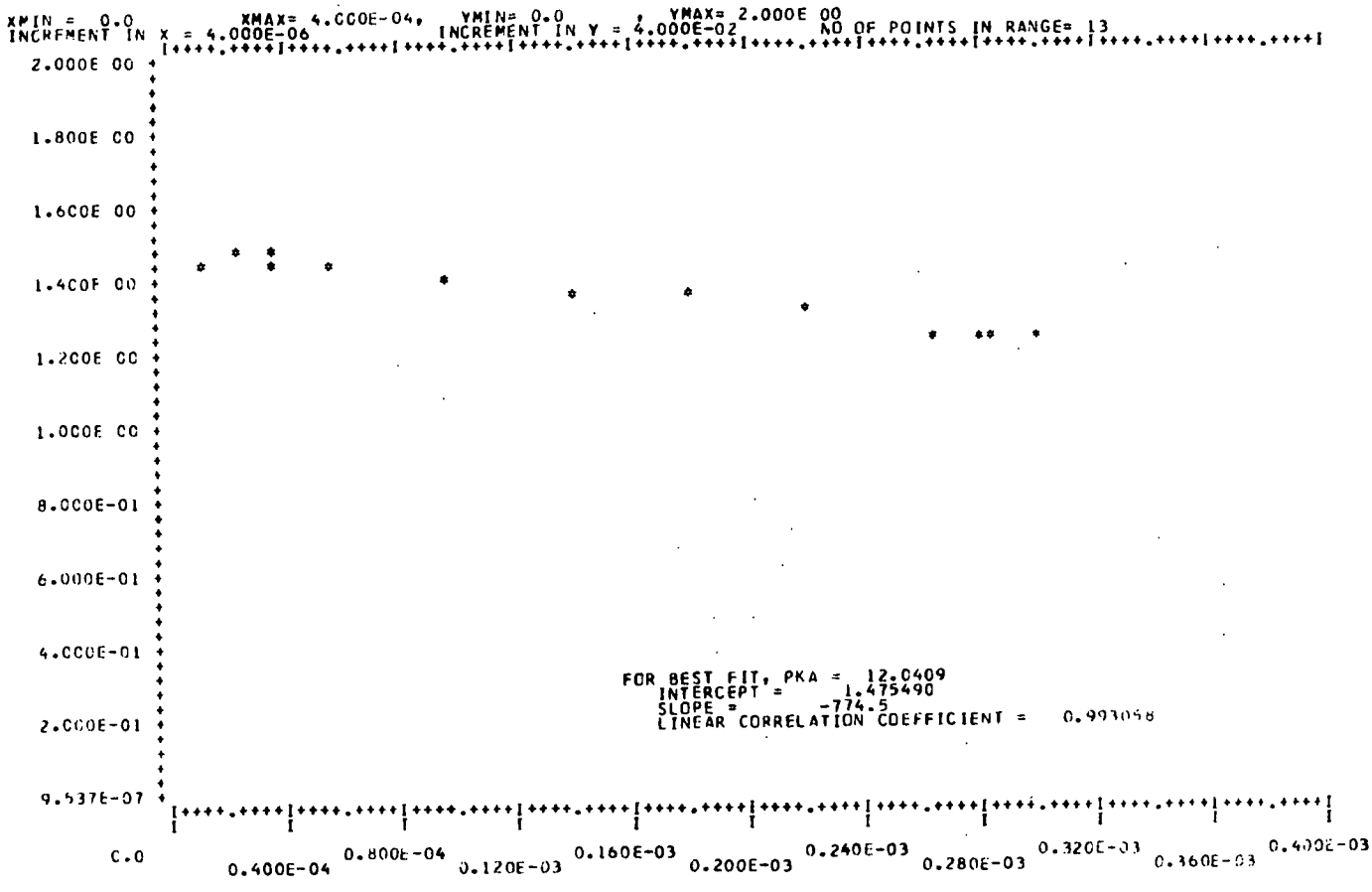


Figure 32. Plot of Data for Determination of pKa2 in 0.92N KCl at 240 nm and 40 Degrees

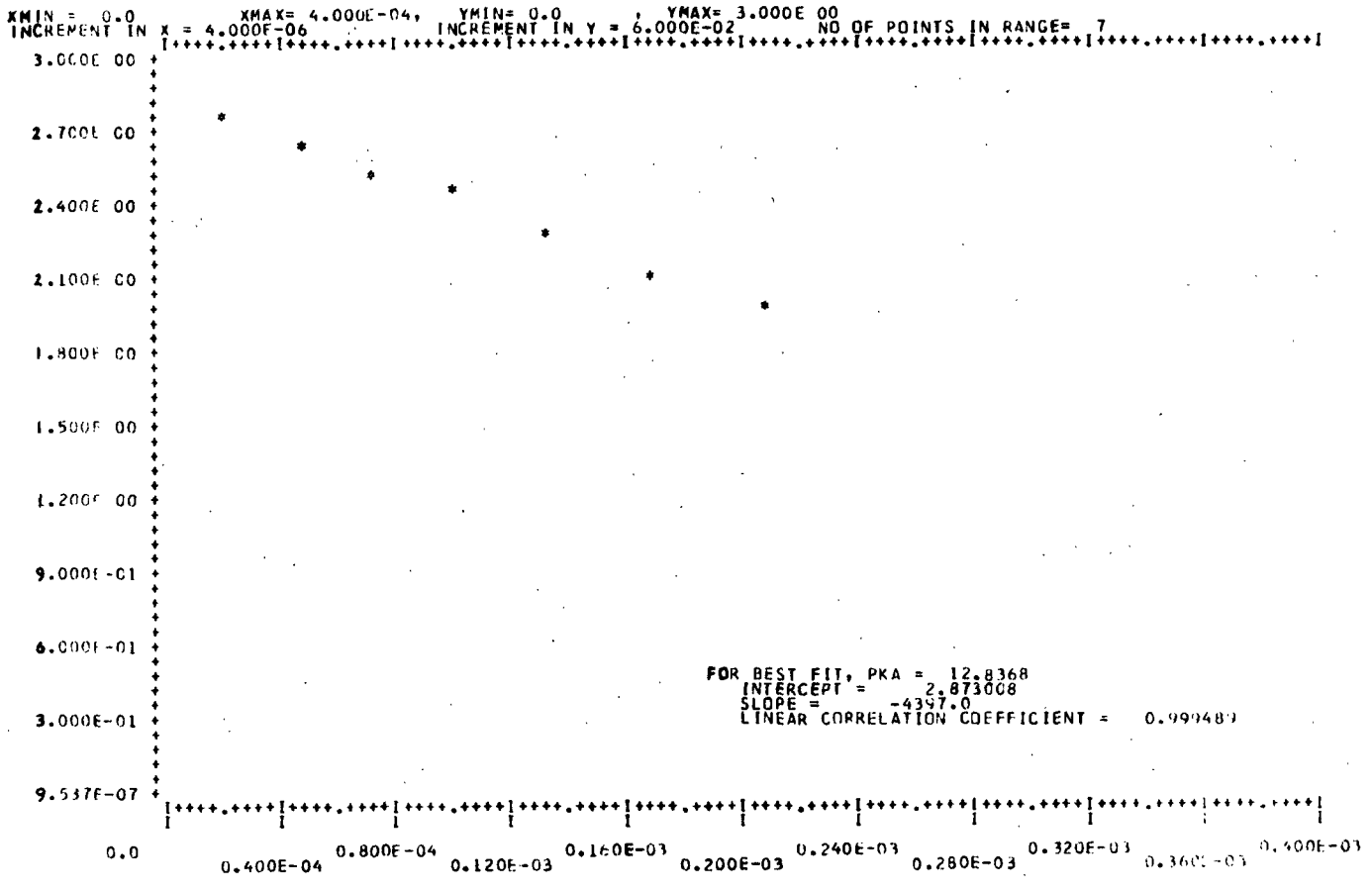


Figure 33. Plot of Data for Determination of pKa2 in 0.1N KCl at 255 nm and 20 Degrees

ionic species of KC4S present in each sample, as the pKas of KC4S are about 4 pH units apart). The program then plots the points (internally) and calculates a correlation coefficient for a straight line [as would be expected from Eq. (19) or (27)]. The pKa value is then increased by a small increment and the calculations repeated. The pKa value for which the best correlation coefficient was obtained was taken to be the best value. This method was checked using a known compound (phenol) and against fabricated data to insure its accuracy.

One potentiometric determination of pKa1 was done. The result from that titration is plotted along with the spectroscopic determination of pKa1 in Fig. 34. Table IX contains the data from which the pKa values were calculated.

TABLE IX

DATA FROM WHICH ACID DISSOCIATION CONSTANTS FOR KC4S WERE DETERMINED

pKa1 (0.1N KCl, 255 nm)

20° Absorption	pH	40° Absorption	pH	60° Absorption	pH	80° Absorption	pH
0.651	7.722	0.274	6.900	0.393	7.099	0.269	6.793
0.967	8.067	0.643	7.546	0.548	7.378	0.425	6.985
1.302	8.319	0.938	7.777	0.938	7.690	0.586	7.266
1.665	8.544	1.266	8.048	1.221	7.868	0.856	7.470
1.928	8.709	1.614	8.240	1.511	8.070	1.148	7.693
2.245	8.933	1.905	8.456	1.790	8.247	1.403	7.853
2.498	9.182	2.190	8.637	2.026	8.421	1.681	8.011
2.674	9.443	2.392	8.813	2.314	8.645	1.894	8.156
2.799	9.826	2.568	9.018	2.442	8.808	2.145	8.351
		2.740	9.324	2.628	9.098	2.323	8.523
						2.472	8.730
						2.593	8.971

pKa2 (0.92N KCl, 255 nm)

2.603	11.635	2.713	10.976	2.678	10.531	2.596	10.460
2.503	11.821	2.511	11.403	2.580	10.938	2.485	10.810
2.339	12.058	2.440	11.619	2.468	11.211	2.371	11.109
2.008	12.433	2.320	11.796	2.290	11.480	2.255	11.318
1.820	12.858	2.127	11.997	2.135	11.640	2.079	11.530
1.689	13.051	1.993	12.191	1.960	11.850	1.826	11.804
1.541	13.521	1.800	12.429	1.727	12.111	1.628	12.100
1.500	13.936	1.638	12.733	1.559	12.369	1.526	12.300
		1.525	13.013	1.487	12.492	1.450	12.367
		1.456	13.313	1.434	12.622		

pKa2 (0.92N KCl, 240 nm)

5° Absorption	pH	20° Absorption	pH	40° Absorption	pH
1.529	11.300	1.541	10.648	1.460	10.635
1.499	11.630	1.555	11.102	1.465	10.968
1.400	12.228	1.525	11.223	1.430	11.141
1.204	12.933	1.524	11.474	1.464	11.159
1.033	13.877	1.506	11.545	1.432	11.363
1.470	11.938	1.483	11.823	1.401	11.665
1.293	12.649	1.420	12.049	1.363	11.935
1.126	13.258	1.427	12.078	1.344	12.158
1.046	14.629	1.357	12.351	1.311	12.390
		1.349	12.372	1.258	12.737
		1.270	12.648	1.251	12.986
		1.257	12.675	1.250	12.930
		1.200	12.965	1.258	13.241
		1.159	13.047		
		1.162	13.994		

TABLE IX (Continued)

DATA FROM WHICH ACID DISSOCIATION CONSTANTS FOR KC4S WERE DETERMINED

pKa2 (0.1N KCl, 255 nm)

20° Absorption	pH
2.786	11.678
2.651	12.099
2.546	12.315
2.431	12.488
2.304	12.691
2.123	12.881
1.952	13.117

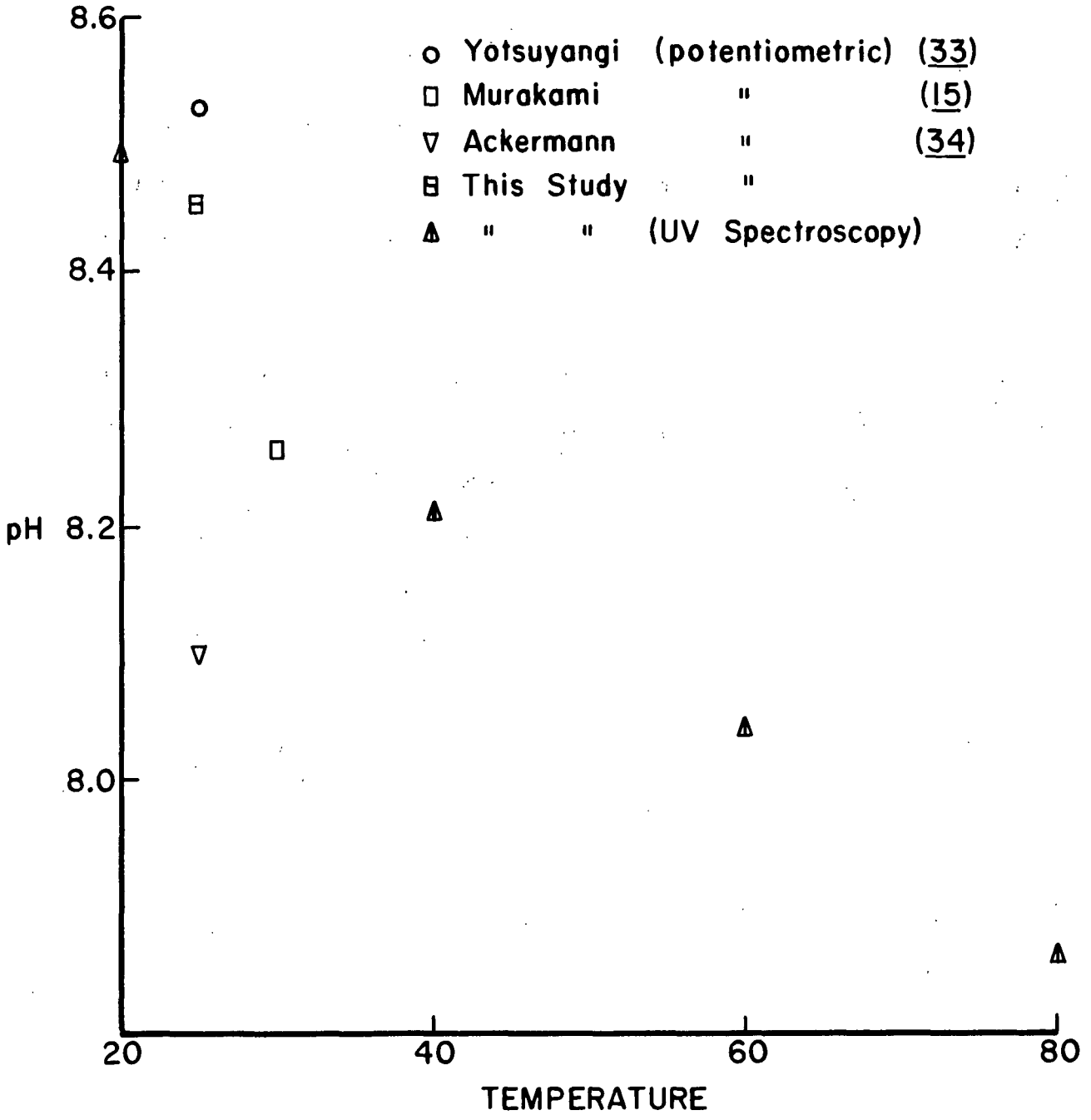


Figure 34. Plot of First Acid Dissociation Constants (pKal's) of KC4S as Determined in this Study and Others at 0.1N Ionic Strength

APPENDIX III

DETERMINATION OF CONFIDENCE LIMITS

It is desirable to have an idea as to how reliable the experimentally determined values of the acid dissociation constants of KC4S and the stability constants of the calcium complex of KC4S are. To this end, an error analysis was done on selected data using a statistical approach.*

The method involved first obtaining a polynomial fit to the experimental data using one of several regression programs available. The function which gave the best fit to the data was then used to generate a sum of the squares and cross products matrix which was inverted to obtain the Gaussian multipliers (c's). These, along with the residual mean square (s_E^2) were used to compute the 95% confidence limits in the absorption measurements for each point from Eq. (28) and (29) from Dunn and Clark (50).

$$y' = s_E^2 (1/n + c_{11}x_1^2 + c_{12}x_1x_2 + c_{21}x_2x_1 + c_{22}x_2^2 \ldots c_{kk}x_k^2) \qquad (28)$$

where:

y' = the estimated variance of the measurement

n = the number of data points

x = the difference between that x term for an individual data point and the average value for that x term for all the data points

and,

$$Y_{0.95} = Y \pm t\,[0.975;\ \gamma]\ \sqrt{y'} \qquad (29)$$

where:

$Y_{0.95}$ = 95% confidence limits

t = students t test value

γ = degrees of freedom (DF2)

*The criteria for employing this method are that each data point is independent and unbiased.

As the stability constants are determined based on a calculated value for the second acid dissociation constant of KC4S, they are sensitive to changes in that calculated pKa2 value. Therefore, in addition to the statistical treatment outlined below, a determination of the sensitivity of the calculated K_{ML} value on the pKa2 value used was done. Results from this analysis are noted in the final paragraph of Appendix III.

Following are the programs, complete with the input and output data from which the 95% confidence limits were determined for the stability constant value at 20°C. (The data at 20°C were chosen as typical data because they gave average fits in both the pKa and stability constant determinations.)

The multiple regression analysis program (MRP — in IPC Library) gave the following function to fit the experimental data. (These data are listed in Appendix VII).

```
THE VARIABLES INCLUDED IN ANALYSIS (Y IS LAST)
 2  3  6  8  1

 THE AVERAGES AND VARIANCES FOR THE VARIABLES

   2  0.11725771D 02   0.26744482D 01
   3 -0.77684571D 01   0.61229075D 02
   6  0.62098329D 02   0.13842069D 05
   8  0.73054154D 03   0.20388823D 07

                                                              R(X)
 I        B(I)              SE(I)              T          ANALYSIS OF X( 1)

 2  -0.3909490 00    0.5611080-01        6.967439          0.954547
 3  -0.5411230 00    0.3869390-01       13.984717          0.995825
 6  -0.4819540-01    0.9580840-02        5.030394          0.999699
 8   0.1809590-02    0.7263440-03        2.491368          0.999644

CONSTANT=   0.3265820 01   TSS=   0.9807110 00   SSW=   0.1148180-01
F=     633.11   DF1=   4   DF2=  30    RSQ=     0.99
```

Where:

1 = Absorbance

2 = pH

3 = ln(Calcium concentration)

6 = $(\ln(\text{Calcium concentration}))^2$

8 = $(\ln(\text{Calcium concentration}))^2$ x pH

The output from the MRP program also gives the average value of each variable (which are called XBAR in CONLIM) and provides the information from which residual mean square is determined (s_E^2 = SSW/DF2).

The pH and ln(calcium concentration) data (Fig. 35) were then inputted into MATRIX (Fig. 36) which formed a sum of the squares and cross products matrix from it and called subroutine DSINV (IBM Scientific Subroutine Package) to invert it. The results of that inversion are shown in Fig. 37.

```
/DATA
11.655          -8.047
11.657          -7.354
11.642          -5.745
11.336          -9.433
11.864          -9.433
12.299          -9.433
11.678          -8.740
12.153          -8.740
11.668          -7.354
11.648          -7.354
11.287          -5.745
11.625          -5.745
11.310          -5.745
11.467          -5.745
11.707          -5.745
11.838          -5.745
11.608          -6.032
11.818          -6.032
11.495          -8.740
11.651          -8.740
11.687          -8.740
11.721          -8.740
11.845          -8.740
11.937          -8.740
12.507          -8.740
11.633          -9.433
11.797          -9.433
12.509          -9.433
11.609          -7.354
11.633          -7.354
11.665          -7.354
11.454          -8.047
11.567          -8.047
11.668          -8.047
11.768          -8.047
```

Figure 35. Input Data for MATRIX [Left Column is pH Values, Right is ln (Calcium Concentration)]

```
/JOB GO
      DIMENSION X1(35),X2(35),X3(35),X4(35)
      DIMENSION A(100)
      DOUBLE PRECISION A,D,X1,X2,X3,X4
      N = 35
      DO 10 I = 1,35
   10 READ (5,100) X1(I), X2(I)
  100 FORMAT (2F10.5)
      DO 11 L = 1,35
      X3(L) = X2(L) * X2(L)
   11 X4(L) = X3(L) * X1(L)
      DO 12 I = 1,35
   12 A(I) = 0.
      A(1) = N
      DO 13 K = 1,35
      A(2) = A(2) + X1(K)
      A(4) = A(4) + X2(K)
      A(7) = A(7) + X3(K)
      A(11)= A(11)+ X4(K)
      A(3) = A(3) + X1(K)*X1(K)
      A(5) = A(5) + X1(K)*X2(K)
      A(8) = A(8) + X1(K)*X3(K)
      A(12)= A(12) + X1(K)*X4(K)
      A(6) = A(6) + X2(K)*X2(K)
      A(9) = A(9) + X2(K)*X3(K)
      A(13) = A(13) + X2(K)*X4(K)
      A(10) = A(10) + X3(K)*X3(K)
      A(14) = A(14) + X3(K)*X4(K)
      A(15) = A(15) + X4(K)*X4(K)
   13 CONTINUE
      K = 5
      WRITE (6,202)
  202 FORMAT(///,'THE MATRIX OF THE SUMS IS...')
      WRITE (6,201)(A(I),I=1,15)
  201 FORMAT(/5E15.8)
      CALL DSINV(A,K,.CC0005,IER)
      WRITE (6,203)
  203 FORMAT(///,'THE INVERSE OF THE MATRIX IS...')
      WRITE (6,201)(A(I),I=1,15)
      CALL EXIT
      END
```

Figure 36. Computer Program MATRIX

```
/IC 940C0600
/JOB GO
BPS FORTRAN D COMPILER
                    SIZE OF COMMON  00000     PROGRAM  02996
END OF COMPILATION  MAIN
BPS FORTRAN D COMPILER
                    SIZE OF COMMON  0C000     PROGRAM  01080
END OF COMPILATION  DSINV
BPS FORTRAN D COMPILER
                    SIZE OF COMMON  00000     PROGRAM  00906
END OF COMPILATION  DMFSD
/DATA

THE MATRIX OF THE SUMS IS...
0.35C000C0D C2 0.410406C0D 03 0.481504900 04-0.27189600D 03-0.31936684C 04
0.217344150 04 0.217344150 04 0.255690990 05-0.17802739D 05 0.148809150 06
0.255690990 05 0.300995700 06-0.209730590 06 0.17552427D 07 0.207181900 08

THE INVERSE OF THE MATRIX IS...
0.102417700 04-0.894233070 02 0.819120900 01-0.388311990 01 0.155724390 01
0.391046300 01-0.131970820 C2 0.129977960 01 0.527033870 00 0.239037780 00
0.111392070 01-0.102995110 00-0.228960390-01-0.175123780-01 0.137350850-02
```

$$\begin{array}{cccccc} --- & --- & C_{11} & --- & C_{12} \\ C_{22} & --- & C_{13} & C_{23} & C_{33} \\ --- & C_{14} & C_{24} & C_{34} & C_{44} \end{array}$$

Figure 37. Output from Computer Program MATRIX (Schematic at Bottom Shows the Positions in the Inverted Matrix Which Correspond to the Gaussian Multipliers)

The Gaussian multipliers were taken from the inverted matrix in Fig. 37 and inputted [along with the pH, ln(calcium concentration) and the absorbance measurement of each sample] into computer program CONLIM which calculated the 95% confidence limits for each absorption measurement by using Eq. (19) and (20). The inputted data is shown in Fig. 38, program CONLIM in Fig. 39 and the output in Fig. 40.

The outputted data was then used in the best fit program (Appendix I) which achieved the best fit to the "95% Confidence" data as if it were real data. The values obtained were then taken to be the confidence limits for the reported stability constant value.

The final cycles from the best fit to the 95% confidence data are shown in Fig. 41. As can be seen, when the high absorption numbers are used, the same value for log K_{ML} (3.86) is obtained as with the original data. The fit is significantly better, however, (0.00356 vs. 0.00611). The low data give a value of log K_{ML} = 3.94. (The G values are gradients which are used internally.)

The log K_{ML} value was recalculated using the 95% confidence limits for pKa2 (12.32 ± 0.11, or 12.21 and 12.43). The results from these determinations showed that when pKa2 = 12.21, log K_{ML} = 12.76, and when pKa2 = 12.43, log K_{ML} = 12.96. On the basis of this, and the statistical limits determined above, the overall 95% confidence limits for log K_{ML} were estimated to be 3.86 ± 0.15 or 3.71 and 4.01.

```
/DATA
8.1912090
1.5572439
1.2997796
-0.10299511
3.9104630
0.52703387
-0.022896039
.23903778
-0.017512378
.00137350B5
11.655     -8.047     1.337
11.657     -7.354     1.234
11.642     -5.745     0.942
11.336     -9.433     1.466
11.864     -9.433     1.389
12.299     -9.433     1.283
11.679     -8.740     1.383
12.153     -8.740     1.257
11.668     -7.354     1.316
11.648     -7.354     1.214
11.287     -5.745     1.062
11.625     -5.745     0.945
11.310     -5.745     1.064
11.467     -5.745     0.999
11.707     -5.745     0.941
11.838     -5.745     0.903
11.608     -6.032     1.002
11.814     -6.032     0.951
11.495     -8.740     1.422
11.651     -8.740     1.389
11.687     -8.740     1.371
11.721     -8.740     1.369
11.845     -8.740     1.338
11.937     -8.740     1.314
12.507     -8.740     1.148
11.633     -9.433     1.434
11.797     -9.433     1.408
12.509     -9.433     1.224
11.609     -7.354     1.251
11.633     -7.354     1.231
11.665     -7.354     1.227
11.454     -8.047     1.392
11.567     -8.047     1.365
11.668     -8.047     1.332
11.768     -8.047     1.303
11.725771 -7.768457 62.098329 730.54154

/END CARD READ, JOB TERMINATED
```

Figure 38. Inputted Data for Computer Program CONLIM (Bottom Values are XBAR's Taken from MRP)

```
/JOB CO
      DIMENSION C(10),X1(35),X2(35),X3(35),X4(35),SMALX1(35),SMALX2(35),
     *SMALX3(35),SMALX4(35),BIGNUM(35),Z(35),SMLNUM(35),ANSWER(35),
     *HIDATA(35),LODATA(35),Y(35)
      DOUBLE PRECISION C,X1,X2,X3,X4,XBAR1,XBAR2,XBAR3,XBAR4,SMALX1,
     *SMALX2,SMALX3,SMALX4,BIGNUM,Z,SMLNUM,ANSWER,HIDATA,LODATA,Y
      DO 10 J = 1,10
   10 READ (5,100) C(J)
      DO 11 J = 1,35
   11 READ (5,101) X1(J),X2(J),Y(J)
      READ (5,102) XBAR1,XBAR2,XBAR3,XBAR4
      DO 12 L = 1,35
      X3(L) = X2(L) * X2(L)
   12 X4(L) = X3(L) * X1(L)
      DO 13 K = 1,35
      SMALX1(K) = X1(K) - XBAR1
      SMALX2(K) = X2(K) - XBAR2
      SMALX3(K) = X3(K) - XBAR3
   13 SMALX4(K) = X4(K) - XBAR4
      DO 14 N = 1,35
   14 BIGNUM(N)=.00038273* ((1./35.) + C(1)*SMALX1(N)**2 + 2. * C(2) *
     *SMALX1(N) * SMALX2(N) + C(3) * SMALX1(N) * SMALX3(N) * 2. + 2. *
     *C(4) * SMALX1(N) * SMALX4(N) + C(5) * SMALX2(N)**2 + C(6) * 2. *
     *SMALX2(N) * SMALX3(N) + C(7) * SMALX2(N) * SMALX4(N) * 2.
     *+ C(8) * SMALX3(N)**2 + C(9) * SMALX3(N) * SMALX4(N) * 2. +
     *C(10) * SMALX4(N)**2)
      DO 15 JJ = 1,35
      Z(JJ) = DABS(BIGNUM(JJ))
      SMLNUM(JJ) = DSQRT(Z(JJ))
      ANSWER(JJ) = 2.042 * SMLNUM(JJ)
      HIDATA(JJ) =  Y(JJ) + ANSWER(JJ)
   15 LODATA(JJ) =  Y(JJ) - ANSWER(JJ)
      WRITE (6,200)
      DO 16 KK = 1,35
   16 WRITE (6,201)  Y(KK)
      WRITE (6,202)
      DO 17 LL = 1,35
   17 WRITE (6,201) HIDATA(LL)
      WRITE (6,204)
      DO 18 MM = 1,35
   18 WRITE (6,201) LODATA(MM)
      WRITE (6,205)
      DO 19 LL = 1,35
   19 WRITE (6,201) BIGNUM (LL)
      WRITE (6,206)
      DO 20 NN = 1,35
   20 WRITE (6,207) SMALX1(NN),SMALX2(NN),SMALX3(NN),SMALX4(NN)
  100 FORMAT (F10.8)
  101 FORMAT (3F10.5)
  102 FORMAT (4F10.5)
  200 FORMAT ('THE ORIGINAL ABSORPTION VALUES ARE...')
  201 FORMAT (F10.5)
  202 FORMAT (/'THE HIGH ABSORPTION VALUES REPRESENTING 95 PERCENT CONFI
     *DENCE LIMITS ARE...')
  204 FORMAT (/'THE LOW ABSORPTION VALUES REPRESENTING 95 PERCENT CONFID
     *ENCE LIMITS ARE...')
  205 FORMAT (//'THE BIGNUMS, CALCULATED INTERNALLY, ARE LISTED BELOW')
  206 FORMAT (//'SMALX1-SMALX4, USED INTERNALLY, ARE LISTED BELOW')
  207 FORMAT (4F15.8)
      CALL EXIT
      END

/END CARD READ, JOB TERMINATED
END OF JOB.
```

Figure 39. Computer Program CONLIM

THE HIGH ABSORPTION VALUES REPRESENTING 95 PERCENT CONFIDENCE LIMITS ARE...	THE ORIGINAL ABSORPTION VALUES ARE...	THE LOW ABSORPTION VALUES REPRESENTING 95 PERCENT CONFIDENCE LIMITS ARE...
1.34733	1.337C0	1.32667
1.24541	1.234C0	1.22259
0.95661	0.942C0	0.92739
1.49049	1.466C0	1.44151
1.40359	1.389C0	1.37441
1.30268	1.283C0	1.26332
1.39229	1.383C0	1.37371
1.26980	1.257C0	1.24420
1.32742	1.316C0	1.30458
1.22542	1.214C0	1.20258
1.08607	1.062C0	1.03793
0.95930	0.945C0	0.93070
1.08682	1.064C0	1.04118
1.01477	0.999C0	0.98323
0.95750	0.941C0	0.92450
0.92557	0.903C0	0.88043
1.01339	1.002C0	0.99061
0.969C0	0.951C0	0.933C0
1.43412	1.422C0	1.40988
1.39860	1.389C0	1.37940
1.38020	1.371C0	1.36180
1.37791	1.369C0	1.36009
1.34666	1.338C0	1.32934
1.32331	1.314C0	1.30469
1.16903	1.148C0	1.12697
1.45136	1.434C0	1.41664
1.42302	1.408C0	1.39298
1.24911	1.224C0	1.19889
1.26259	1.251C0	1.23941
1.24246	1.231C0	1.21954
1.23842	1.227C0	1.21558
1.40480	1.392C0	1.37920
1.37605	1.365C0	1.35395
1.34228	1.332C0	1.32172
1.31344	1.303C0	1.29256

Figure 40. Output from Program CONLIM

Low Data

```
F =   0.1349363D-01   G(1) =   0.9841851D-02   G(2) =  -0.4934831D-01
X(1) =      3.93826   X(2) =     3.39234
F =   0.7816454D-01   G(1) =  -0.5532646D 00   G(2) =   0.2699227D 01
X(1) =      3.92872   X(2) =     3.44169
F =   0.1346744D-01   G(1) =  -0.3283255D-02   G(2) =  -0.3259528D-03
X(1) =      3.93806   X(2) =     3.39337
F =   0.1346044D-01   G(1) =  -0.1163289D-02   G(2) =   0.4071023D-03
X(1) =      3.94121   X(2) =     3.39417
F =   0.1346072D-01   G(1) =   0.8926668D-03   G(2) =   0.1402006D-02
X(1) =      3.94437   X(2) =     3.39502
F =   0.1345966D-01   G(1) =  -0.1986480D-03   G(2) =   0.8371799D-03
X(1) =      3.94268   X(2) =     3.39457
F =   0.1345966D-01   G(1) =  -0.2167054D-03   G(2) =   0.8297241D-03
X(1) =      3.94265   X(2) =     3.39457
F =   0.1345966D-01   G(1) =  -0.2049965D-03   G(2) =   0.8340321D-03
X(1) =      3.94267   X(2) =     3.39457
F =   0.1345966D-01   G(1) =  -0.2002757D-03   G(2) =   0.8369865D-03
X(1) =      3.94268   X(2) =     3.39457
F =   0.1345966D-01   G(1) =  -0.1989250D-03   G(2) =   0.8380944D-03
X(1) =      3.94268   X(2) =     3.39457
F =   0.1345966D-01   G(1) =  -0.1984899D-03   G(2) =   0.8384905D-03
X(1) =      3.94268   X(2) =     3.39457
```

High Data

```
F =   0.3595776D-02   G(1) =  -0.2462370D-02   G(2) =   0.2565295D-01
X(1) =      3.87059   X(2) =     3.40713
F =   0.1745526D-01   G(1) =   0.3116769D 00   G(2) =  -0.1046858D 01
X(1) =      3.87305   X(2) =     3.39143
F =   0.3579666D-02   G(1) =   0.4102193D-02   G(2) =   0.3591493D-03
X(1) =      3.87064   X(2) =     3.40657
F =   0.3567036D-02   G(1) =   0.1601725D-02   G(2) =   0.4472508D-03
X(1) =      3.86671   X(2) =     3.40555
F =   0.3565208D-02   G(1) =  -0.9987477D-03   G(2) =   0.9152143D-03
X(1) =      3.86278   X(2) =     3.40453
F =   0.3564733D-02   G(1) =  -0.1722218D-03   G(2) =   0.7271694D-03
X(1) =      3.86402   X(2) =     3.40485
F =   0.3564733D-02   G(1) =  -0.1292682D-03   G(2) =   0.7317057D-03
X(1) =      3.86399   X(2) =     3.40485
F =   0.3564733D-02   G(1) =  -0.1749898D-03   G(2) =   0.7285754D-03
X(1) =      3.86401   X(2) =     3.40485
F =   0.3564733D-02   G(1) =  -0.1727307D-03   G(2) =   0.7277723D-03
X(1) =      3.86401   X(2) =     3.40485
F =   0.3564733D-02   G(1) =  -0.1721109D-03   G(2) =   0.7280040D-03
X(1) =      3.86402   X(2) =     3.40485
F =   0.3564733D-02   G(1) =  -0.1717454D-03   G(2) =   0.7271694D-03
X(1) =      3.86402   X(2) =     3.40485
F =   0.3564733D-02   G(1) =  -0.1722218D-03   G(2) =   0.7271694D-03
X(1) =      3.86402   X(2) =     3.40485
F =   0.3564733D-02   G(1) =  -0.1722218D-03   G(2) =   0.7271694D-03
X(1) =      3.86402   X(2) =     3.40485
F =   0.3564733D-02   G(1) =  -0.1722218D-03   G(2) =   0.7271694D-03
X(1) =      3.86402   X(2) =     3.40485
F =   0.3564733D-02   G(1) =  -0.1722218D-03   G(2) =   0.7271694D-03
X(1) =      3.86402   X(2) =     3.40485
```

Figure 41. Final Cycles as the Best Fit Routine Seeks to Determine the Best Values for log K_{ML} (X(1)) and log ε_{ML} (X(2)) for the 95% Confidence Data

APPENDIX IV

STATISTICAL F-TEST

As noted on page 41, when only one complex species (ML) was assumed to exist in the experimental system at 20°C the fit (as described on page 41) was found to equal 0.00611. When two complexes (ML and ML_2) were assumed to exist, the fit achieved was 0.00473. The variance associated with these fits was calculated by dividing the fit (sum of the squares) by the degrees of freedom (35 samples - 2 constraints for one complex, 35 - 3 for two complexes). The variances were found to be $0.00611/33 = 1.852 \times 10^{-4}$ for one complex, and $0.00473/32 = 1.478 \times 10^{-4}$ for two complexes.

The variance due to experimental error was estimated according to Volk (51) from 22 pairs of duplicate samples and two sets of triplicate samples* to be 0.000174. The F values were then computed to be:

For ML

$$F = \frac{1.852 \times 10^{-4}}{1.74 \times 10^{-4}} = 1.06$$

For ML and ML_2

$$F = \frac{1.478 \times 10^{-4}}{1.74 \times 10^{-4}} = 0.85$$

Using a standard F table (52), it can be determined that 1.06 falls within the 0.95 limit (about 1.95 for 33 and 23 degrees of freedom), and therefore, that the discrepancy between the calculated and the experimental data when one complex (ML) is assumed, can be explained on the basis of experimental error. While a better fit is achieved when two complexes are assumed, it cannot be determined on the basis of the F-test that this improvement indicates that a second complex exists in the experimental system.

*These are the samples listed in Appendix VII which had the same contents and were analyzed at the same temperature.

The F-test results were similar for the data at 40, 60 and 80°C. While the variance associated with the data was 5° when one complex was assumed was greater than the 0.95 limit, it was within the 0.99 limit. Assuming a second complex existed in the experimental system at 5° did not decrease the variance.

APPENDIX V

3D PLOTS EXPRESSING IONIC CALCIUM CONCENTRATION AS A FUNCTION OF TEMPERATURE AND BASE CONCENTRATION

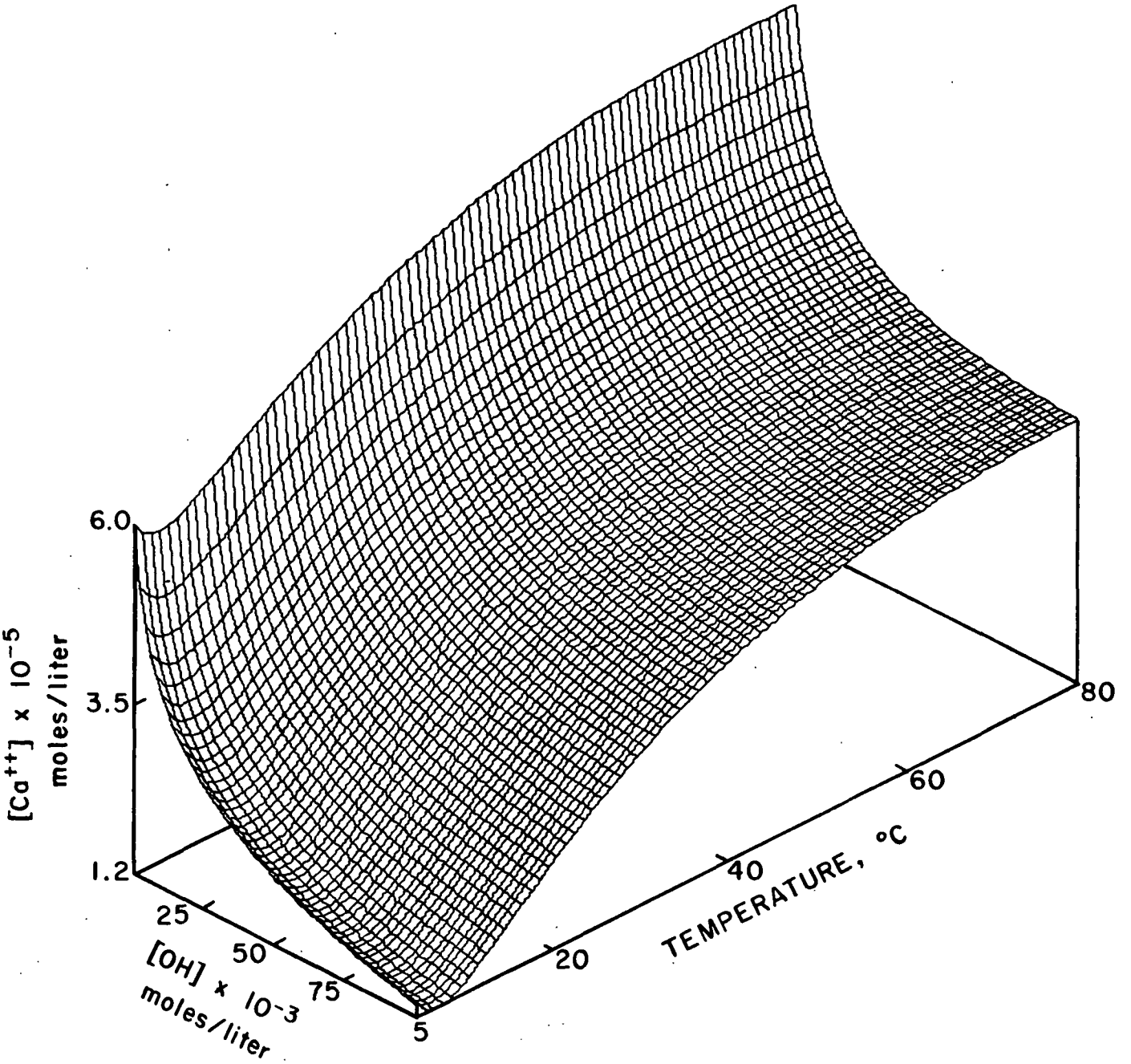


Figure 42. Variation of Ionic Calcium with Base Concentration and Temperature. [0.92N Ionic Strength (KCl), Molar Ratio of Calcium:KC4S of 1:4]

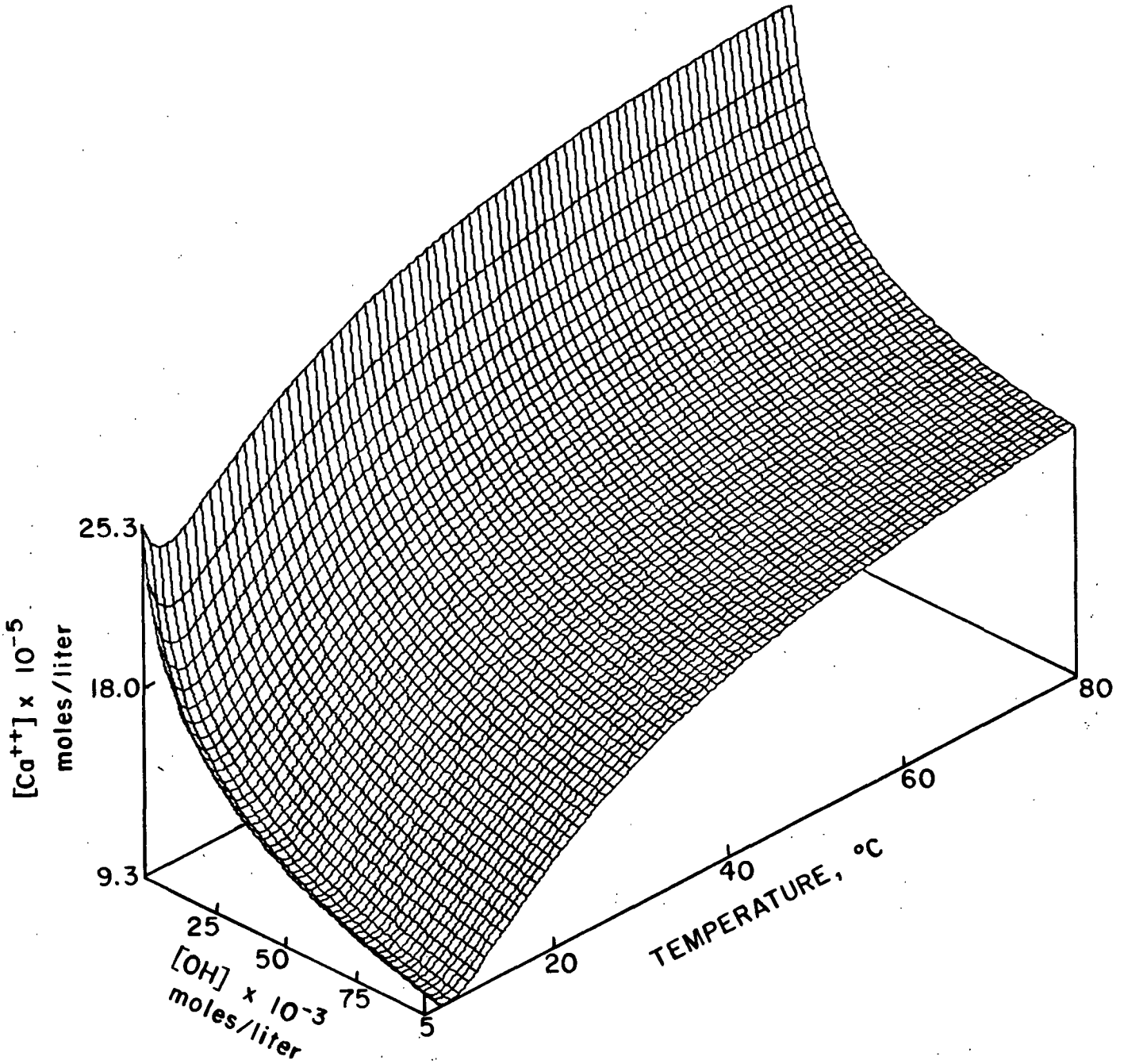


Figure 43. Variation of Ionic Calcium with Base Concentration and Temperature. [0.92N Ionic Strength (KCl), Molar Ratio of Calcium:KC4S of 1:1]

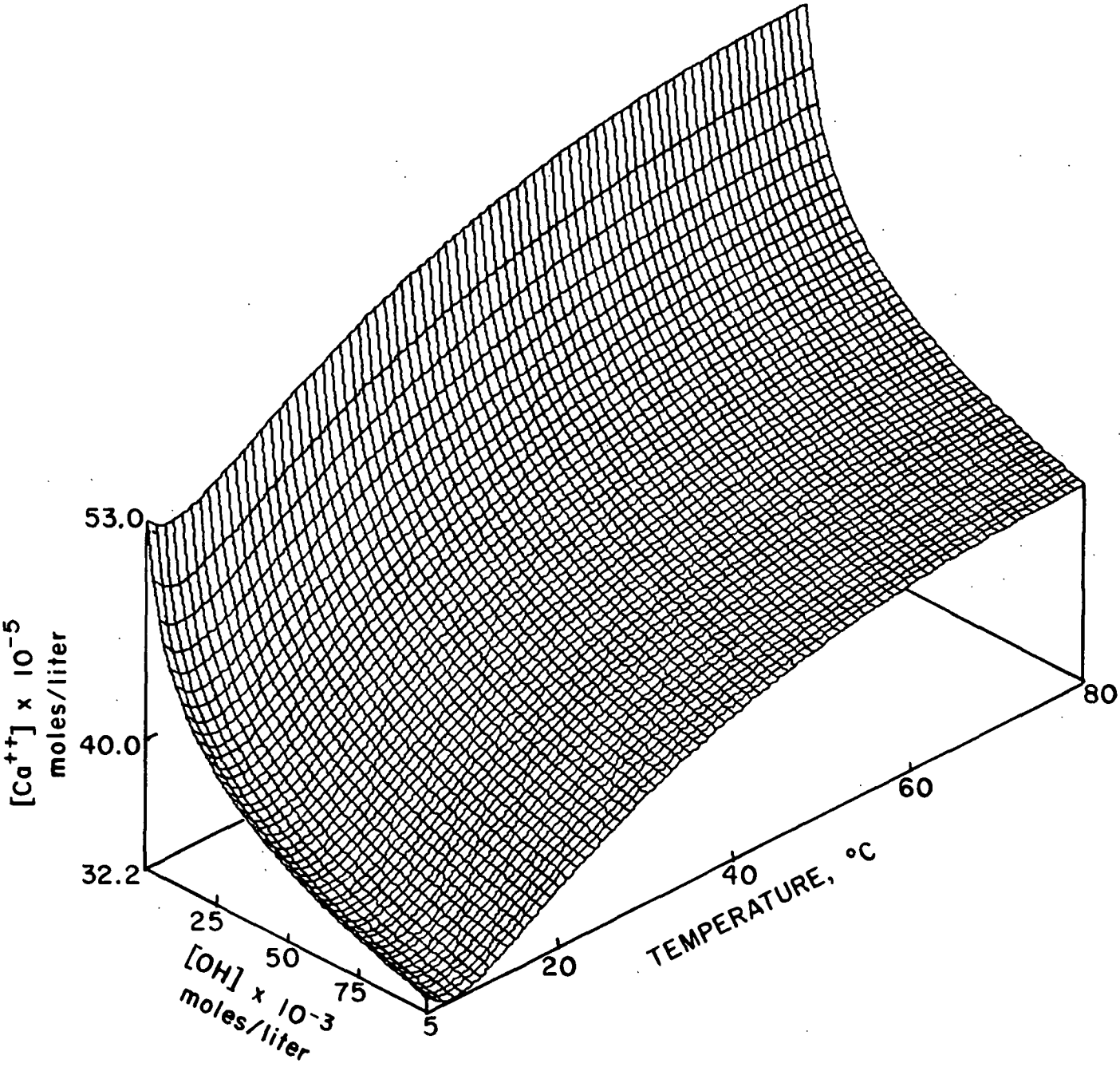


Figure 44. Variation of Ionic Calcium with Base Concentration and Temperature. [0.92N Ionic Strength (KCl), Molar Ratio of Calcium:KC4S of 2:1]

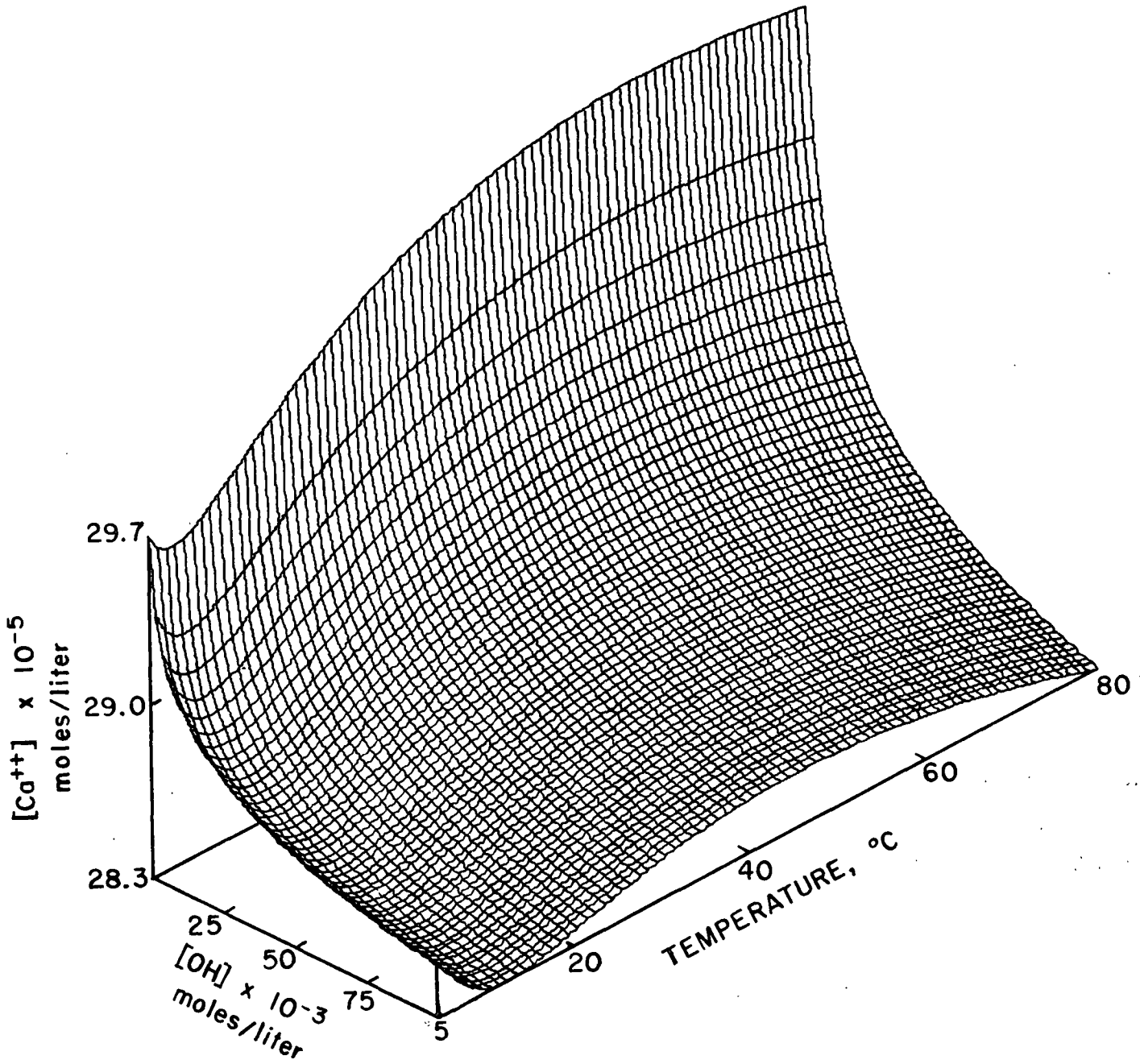
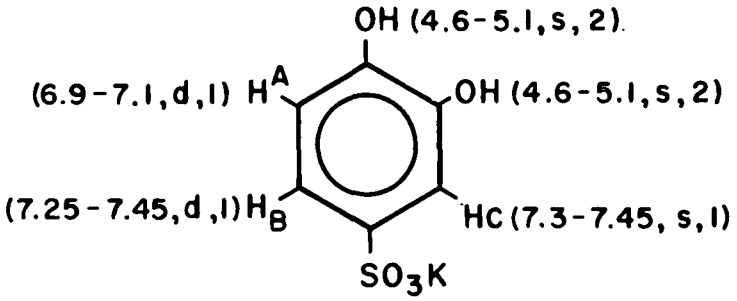


Figure 45. Variation of Ionic Calcium with Base Concentration and Temperature. [0.92N Ionic Strength (KCl), Molar Ratio of Calcium:KC4S of 10:1]

APPENDIX VI

PROTON NUCLEAR MAGNETIC RESONANCE DATA

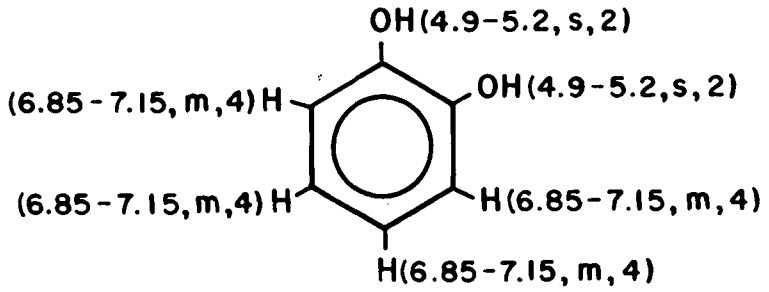
KC4S



[peak location, structure (s = singlet, d = doublet, m = multiplet), integral]

KC4S was analyzed with D_2O as the solvent. Shifts (δ) are measured against DSS (4,4-dimethyl 4-silapentane sodium sulfonate) reference. Protons A and B are strongly coupled. Hydroxyl protons appear with water impurity. Appearance of two downfield aromatic protons indicates substitution took place at the 4 position.

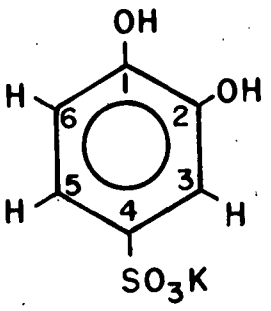
CATECHOL



Catechol was analyzed with D_2O as the solvent. Shifts are based on DSS reference. Aromatic protons are strongly coupled. Hydroxyl protons appear with water impurity.

^{13}C-NUCLEAR MAGNETIC RESONANCE DATA*

KC4S

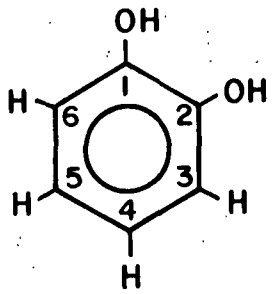


KC4S was analyzed with D_2O as the solvent. The shifts are based on DSS reference.

	Assignment (ppm)
C-1	149.4
C-2	146.2
C-3	115.8
C-4	137.0
C-5	121.1
C-6	118.3

(Assigned with standard tables.)

CATECHOL



Catechol was analyzed with D_2O as the solvent. The shifts are based on DSS reference.

	Assignment (ppm)
C-1,2	146.2
C-3,6	118.8
C-4,5	123.5

(Assigned with standard tables.)

*Complete decoupling.

APPENDIX VII

DATA FROM WHICH STABILITY CONSTANTS WERE DETERMINED

Sample	Calcium Concentration	Base Concentration	Absorption	pH
1	0.00008	0.001	1.465	11.557
2	0.00008	0.002	1.402	11.932
3	0.00008	0.003	1.351	12.225
4	0.00008	0.006	1.276	12.442
5	0.00008	0.002	1.426	11.885
6	0.00008	0.006	1.292	12.400
7	0.00008	0.0008	1.528	11.398
8	0.00008	0.003	1.403	12.111
9	0.00016	0.004	1.319	12.248
10	0.00016	0.008	1.219	12.572
11	0.00016	0.012	1.158	12.765
12	0.00016	0.001	1.450	11.580
13	0.00032	0.001	1.405	11.535
14	0.00032	0.006	1.110	12.429
15	0.00032	0.002	1.323	11.885
16	0.00032	0.006	1.134	12.408
17	0.00032	0.0008	1.459	11.467
18	0.00064	0.004	1.105	12.230
19	0.00064	0.012	0.957	12.745
20	0.00064	0.001	1.345	11.515
21	0.00064	0.002	1.248	11.878
22	0.00320	0.006	0.831	12.417
23	0.00320	0.001	1.078	11.455
24	0.00320	0.002	0.945	11.883
25	0.00320	0.001	1.093	11.503
26	0.00320	0.0006	1.263	11.120

Figure 46. Samples from Which Stability Constants were Determined at 5°C. (Concentrations are Expressed in Moles/Liter at 20°C. All Solutions had KC4S Concentrations of 0.00032 Molar at 20°C. Absorption Measurements were Made at 240 nm. Sample Size was 50 mL. Ionic Strength was 0.92N KCl)

Sample	Calcium Concentration	Base Concentration	Absorption	pH
1	0.00008	0.004	1.434	11.633
2	0.00008	0.006	1.408	11.797
3	0.00008	0.030	1.224	12.509
4	0.00008	0.002	1.466	11.336
5	0.00008	0.006	1.389	11.864
6	0.00008	0.016	1.283	12.299
7	0.00016	0.0034	1.422	11.495
8	0.00016	0.004	1.389	11.651
9	0.00016	0.0046	1.371	11.687
10	0.00016	0.006	1.369	11.721
11	0.00016	0.0066	1.338	11.845
12	0.00016	0.008	1.314	11.937
13	0.00016	0.030	1.148	12.507
14	0.00016	0.004	1.383	11.678
15	0.00016	0.012	1.257	12.153
16	0.00032	0.0034	1.392	11.454
17	0.00032	0.0040	1.365	11.567
18	0.00032	0.0046	1.332	11.668
19	0.00032	0.0060	1.303	11.768
20	0.00032	0.004	1.316	11.668
21	0.00032	0.004	1.337	11.655
22	0.00064	0.004	1.251	11.609
23	0.00064	0.005	1.231	11.633
24	0.00064	0.006	1.227	11.665
25	0.00064	0.004	1.214	11.648
26	0.00064	0.004	1.234	11.657
27	0.00240	0.004	1.002	11.608
28	0.00240	0.006	0.951	11.814
29	0.0032	0.002	1.064	11.310
30	0.0032	0.0036	0.999	11.467
31	0.0032	0.0046	0.941	11.707
32	0.0032	0.006	0.903	11.838
33	0.0032	0.002	1.062	11.287
34	0.0032	0.004	0.945	11.625
35	0.0032	0.004	0.942	11.642

Figure 47. Samples from Which Stability Constants were Determined at 20°C. (Conditions the same as noted in Figure 46)

Sample	Calcium Concentration	Base Concentration	Absorption	pH
1	0.00008	0.02	1.358	11.663
2	0.00008	0.02	1.355	11.664
3	0.00008	--	1.300	11.988
4	0.00008	0.006	1.410	11.131
5	0.00016	0.006	1.406	11.155
6	0.00016	0.02	1.320	11.668
7	0.00016	0.006	1.409	11.137
8	0.00016	0.02	1.307	11.664
9	0.00032	0.006	1.359	11.125
10	0.00032	0.02	1.238	11.664
11	0.00032	0.006	1.357	11.121
12	0.00032	0.02	1.237	11.667
13	0.00064	0.006	1.274	11.092
14	0.00064	0.006	1.260	11.116
15	0.00064	0.02	1.114	11.663
16	0.00064	0.02	1.112	11.665
17	0.00320	0.006	1.006	11.111
18	0.00320	0.02	0.892	11.654
19	0.00320	0.006	1.007	11.145
20	0.00320	0.02	0.903	11.664

Figure 48. Samples from Which Stability Constants were Determined at 40°C. (Conditions the same as noted in Figure 46)

Sample	Calcium Concentration	Base Concentration	Absorption	pH
1	0.00008	0.010	1.430	10.852
2	0.00008	0.014	1.429	11.028
3	0.00008	0.024	1.415	11.248
4	0.00008	0.040	1.402	11.454
5	0.00016	0.010	1.413	10.848
6	0.00016	0.014	1.407	10.999
7	0.00016	0.024	1.366	11.237
8	0.00016	0.040	1.351	11.450
9	0.00032	0.010	1.374	10.854
10	0.00032	0.020	1.327	11.138
11	0.00032	0.040	1.285	11.445
12	0.00064	0.010	1.296	10.840
13	0.00064	0.040	1.162	11.405
14	0.00320	0.01	1.061	10.873
15	0.00320	0.04	0.962	11.424
16	0.00320	0.004	1.185	10.494
17	0.00320	0.020	0.994	11.124

Figure 49. Samples from Which Stability Constants were Determined at 60°C. (Conditions the same as noted in Figure 46)

Sample	Calcium Concentration	Base Concentration	Absorption	pH
1	0.00008	0.02	1.422	10.926
2	0.00008	0.10	1.427	11.306
3	0.00008	0.02	1.438	10.985
4	0.00008	0.10	1.439	11.520
5	0.00008	0.008	1.424	10.532
6	0.00016	0.008	1.413	10.539
7	0.00016	0.020	1.395	10.894
8	0.00016	0.100	1.400	11.593
9	0.00032	0.04	1.326	11.158
10	0.00032	0.08	1.312	11.477
11	0.00032	0.04	1.333	11.250
12	0.00032	0.08	1.319	11.459
13	0.00032	0.008	1.388	10.539
14	0.00032	0.02	1.358	10.886
15	0.00064	0.008	1.350	10.490
16	0.00064	0.02	1.290	10.873
17	0.00064	0.04	1.258	11.247
18	0.00064	0.10	1.216	11.640
19	0.0032	0.02	1.084	10.850
20	0.0032	0.08	1.019	11.509
21	0.0032	0.006	1.199	10.347

Figure 50. Samples from Which Stability Constants were Determined at 80°C. (Conditions the same as Noted in Figure 46.)